~~Mae Howe~~
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2510
760

SOLUBILITY OF BASES AND SALTS IN WATER AT 18°

	K	Na	Li	Ag	Tl	Ba	Sr	Ca	Mg	Zn	Pb
Cl	32.95 3.9	35.86 5.42	77.79 13.3	0.0_316 0.0_410	0.3 0.013	37.24 1.7	51.09 3.0	73.19 5.4	55.81 5.1	203.9 9.2	1.49 0.05
Br	65.86 4.6	88.76 6.9	168.7 12.6	0.0_41 0.0_66	0.04 0.0_215	103.6 2.9	96.52 3.4	143.3 5.2	103.1 4.6	478.2 9.8	0.598 0.02
I	137.5 6.0	177.9 8.1	161.5 8.5	0.0_63 0.0_71	0.006 0.0_317	201.4 3.8	169.2 3.9	200 4.8	148.2 4.1	419 6.9	0.08 0.0_22
F	92.56 12.4	4.44 1.06	0.27 0.11	195.4 13.5	72.05 3	0.16 0.0_292	0.012 0.001	0.0016 0.0_32	0.0076 0.0_214	0.005 0.0_35	0.07 0.003
NO_3	30.34 2.6	83.97 7.4	71.43 7.3	213.4 8.4	8.91 0.35	8.74 0.33	66.27 2.7	121.8 5.2	74.31 4.0	117.8 4.7	51.66 1.4
ClO_3	6.6 0.52	97.16 6.4	313.4 15.3	12.25 0.6	3.69 0.13	35.42 1.1	174.9 4.6	179.3 5.3	126.4 4.7	183.9 5.3	150.6 3.16
BrO_3	6.38 0.38	36.67 2.2	152.5 8.20	0.59 0.025	0.30 0.009	0.8 0.02	30.0 0.9	85.17 2.3	42.86 1.5	58.43 1.8	1.3 0.03
IO_3	7.62 0.35	8.33 0.4	80.43 3.84	0.004 0.0_314	0.059 0.0_216	0.05 0.001	0.25 0.0_257	0.25 0.007	6.87 0.26	0.83 0.02	0.002 0.0_43
OH	142.9 18	116.4 21.	12.04 5.0	0.01 0.001	40.04 1.76	3.7 0.22	0.77 0.063	0.17 0.02	0.001 0.0_32	0.0_35 0.0_45	0.01 0.0_34
SO_4	11.11 0.62	16.83 1.15	35.64 2.8	0.55 0.020	4.74 0.09	0.0_323 0.0_410	0.011 0.0_36	0.20 0.015	35.43 2.8	53.12 3.1	0.0041 0.0_313
CrO_4	63.1 2.7	61.21 3.30	111.6 6.5	0.0025 0.0_315	0.006 0.0_31	0.0_338 0.0_415	0.12 0.006	0.4 0.03	73.0 4.3	. . . .	0.0_42 0.0_65
C_2O_4	30.27 1.6	3.34 0.24	7.22 0.69	0.0035 0.0_32	1.48 0.030	0.0086 0.0_338	0.0046 0.0_326	0.0_356 0.0_443	0.03 0.0027	0.0_36 0.0_44	0.0_315 0.0_55
CO_3	108.0 5.9	19.39 1.8	1.3 0.17	0.003 0.0_31	4.95 0.10	0.0023 0.0_311	0.0011 0.0_47	0.0013 0.0_313	0.1 0.01	0.004? 0.0_33?	0.0_31 0.0_43

The *upper number* in each square gives the number of grams of the anhydrous salt held in solution by 100 cc. of water. The *lower number* is the molar solubility, *i.e.*, the number contained in one liter of the saturated solution.

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Molecular wt. of any gas at St. Condition occupies 22.4 liters

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GENERAL CHEMISTRY

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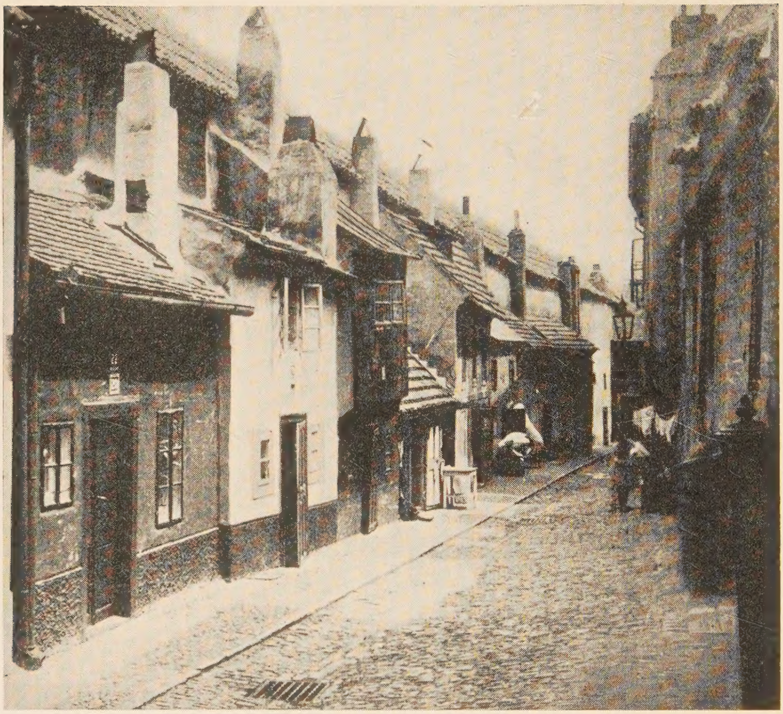

"GOLD ALLEY"

THE STREET OF THE ALCHEMISTS IN PRAGUE

Alchemy dates back nearly two thousand years to the very primitive chemistry of the Egyptians, Greeks, and Arabs. Although it became the pretended art of transmitting lead and other base metals into gold by the magical aid of the Philosophers' Stone, through alchemy many valuable properties, reactions, and chemical methods were discovered and handed down the centuries.

"It was, however, almost from its beginnings so allied with magic, astrology, and superstition and so encrusted with ambiguity, that it soon became in the hands of the unscrupulous an extraordinary agency for preying upon the credulity and avarice of kings and commons alike" (A. D. Little).

In the Middle Ages King Rudolph II of Bohemia welcomed to Prague alchemists and artisans, clairvoyants and charlatans, giving them residence in the dolls' houses of Gold Alley, still to be seen at the back of the royal castle. Here gathered the notorious but brilliant scoundrel John Dee, the impudent rascal Edward Kelley, the great astronomers Kepler and Tycho Brahe, and others, who deceived the king and extracted gold from pockets rather than from lead.

And now, after long-continued ridicule of the alchemists, the modern chemist has actually achieved transmutation of one element into another, in minute quantities.

GENERAL CHEMISTRY

By

HARRY N. HOLMES
PROFESSOR OF CHEMISTRY
IN OBERLIN COLLEGE

Revised Edition

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1930

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PREFACE

After seven or eight years a revision of any text on Chemistry must be radical, yet it is still true of this as of the first edition, that it has been written from the viewpoint of the student and not to impress men who are already good chemists. It is a text in the full sense of the term, not a reference book.

Facts and theories, no matter how imposing the array, can be of no value unless the student is interested. To this end homely illustrations are used and a style far from pedantic employed. Chemistry for College Freshmen should receive very different treatment from Chemistry for more advanced students.

Without apology, the electronic conception of the atom is introduced in the second chapter quite simply and naturally, for the radio has made even high school boys familiar with electrons. A little later, in the chapter on Valence, the electron is used again to make clear the distinction between positive and negative valence. The concept is brought out again in the chapters on Ionization and in optional methods for balancing Oxidation-Reduction equations. Finally an entire chapter on the Structure of the Atom is introduced immediately following the Periodic System. The electronic concept is also employed in the chapter on Electrochemistry.

A comparison, clear and condensed, of the Octet Theory and the modified Bohr Theory of the atom is offered with the warning that the final theory is still in the making.

Since this text is adapted to the needs of students well-trained in preparatory school chemistry it is not out of place to give a very brief introduction to the Debye-Hückel theory of complete ionization. However, this section and that explaining in detail the fractional distillation of water-alcohol mixtures, as well as many other paragraphs and pages set in smaller type, may be omitted, if desired, without really breaking the continuity of treatment.

A year of general chemistry should not be merely a year of fact-stuffing, but rather an introduction to scientific thinking. Consequently Ionization is presented here with the broad view showing the student the parallel between ionization in water, liquid ammonia, phosgene and fused salts. A discussion of neutralization of the acids and bases in these various systems stimulates the imagination of the student.

His vision, his intellectual horizon, is extended still more by the new chapter on Photochemistry, something of an innovation in texts of this type. By photochemistry is here meant something more than photography and photosynthesis, although they are properly included in the treatment.

Nitrogen Fixation now looms so large before the world's eye that it is given a chapter of extended treatment. So, too, is the subject of Fuels. The later developments such as the Bergius "liquefaction of coal" and the recent radical changes in petroleum cracking processes are discussed.

Bacteria as Chemists, in a page or two, and Enzymes in two more, will hold the attention of the class very profitably.

Werner's coordination theory is the last topic in the book, but it may be introduced in connection with chromium or cobalt as well as with platinum.

The lattice structure of crystals or other solids is discussed freely, especially in the chapters on Gases, Liquids and Solids, and Metals and Alloys.

To give students who go on in Chemistry a better preparation, short optional sections are presented on the hydrogen electrode and the meaning of the pH notation (Appendix).

There has been no desire to omit the chapter on Colloid Chemistry for that subject is growing with great speed, nor to give any less attention to the important group of chapters on Organic Chemistry, including Nutrition. These, properly taught, delight the class with the training in logic involved, and with the close relation of the compounds of carbon to daily life.

Many new problems and references as well as nearly a hundred new illustrations add to the value of the revision. As may be inferred, the second edition is a little larger than the first.

Much optional material in fine print has been included, although not essential to a shorter course.

Whatever soundness there may be in this volume I owe to the admirable precept and example of Ira Remsen, during his lifetime the Dean of American teachers of Chemistry.

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Harry N. Holmes

Oberlin College
March, 1930

CONTENTS

CHAPTER		PAGE
I.	BASIC PRINCIPLES	1
II.	THE ATOMIC THEORY	15
III.	SYMBOLS, FORMULAS, AND EQUATIONS	21
IV.	OXYGEN AND OZONE	25
V.	GASES, LIQUIDS, AND SOLIDS	48
VI.	HYDROGEN	70
VII.	VALENCE	87
VIII.	WATER AND HYDROGEN PEROXIDE	96
IX.	CARBON AND ITS OXIDES	109
X.	MOLECULAR AND ATOMIC WEIGHTS	126
XI.	SOLUTIONS	135
XII.	CHLORINE, BROMINE, IODINE, AND FLUORINE	158
XIII.	THE SIMPLE HALOGEN ACIDS	175
XIV.	THE OXYGEN ACIDS OF THE HALOGENS	187
XV.	SODIUM AND SODIUM HYDROXIDE BASES	195
XVI.	IONIZATION	200
XVII.	APPLICATIONS OF THE IONIC THEORY	213
XVIII.	SULFUR AND HYDROGEN SULFIDE	229
XIX.	SULFURIC ACID AND THE OXIDES OF SULFUR	241
XX.	THE PERIODIC SYSTEM. ATOMIC NUMBERS	256
XXI.	STRUCTURE OF THE ATOM. RADIOACTIVITY	267
XXII.	THE ATMOSPHERE. THE ARGON FAMILY	284
XXIII.	EQUILIBRIUM	297
XXIV.	NITROGEN AND AMMONIA	309
XXV.	NITROGEN FIXATION	320
XXVI.	THE OXIDES OF NITROGEN	328
XXVII.	NITRIC AND NITROUS ACIDS AND THEIR SALTS	332
XXVIII.	THE PHOSPHORUS GROUP	346
XXIX.	THE HYDROCARBONS. FUELS	368
XXX.	ALCOHOLS, ACIDS, FATS, AND SOAPS	394
XXXI.	THE CARBOHYDRATES	407
XXXII.	CELLULOSE AND ITS ESTERS. RAYON	415
XXXIII.	FOOD AND NUTRITION	421
XXXIV.	SILICON AND BORON	431
XXXV.	PHOTOCHEMISTRY	442
XXXVI.	COLLOID CHEMISTRY	454
XXXVII.	METALS AND ALLOYS	474
XXXVIII.	THE ALKALI METALS	484

CHAPTER		PAGE
XXXIX.	THE ALKALINE EARTH METALS	502
XL.	COPPER, SILVER AND GOLD	515
XLI.	MAGNESIUM, ZINC, CADMIUM, MERCURY, AND BERYLLIUM	529
XLII.	ELECTROCHEMISTRY	548
XLIII.	ALUMINUM. DYES, CEMENT	557
XLIV.	TIN AND LEAD	573
XLV.	CHROMIUM AND MANGANESE	586
XLVI.	IRON, COBALT, AND NICKEL	599
XLVII.	VANADIUM, MOLYBDENUM, TUNGSTEN, AND URANIUM	621
XLVIII.	THE PLATINUM METALS	627
	APPENDIX	633
	INDEX	641

GENERAL CHEMISTRY

GENERAL CHEMISTRY

CHAPTER I

BASIC PRINCIPLES

What Is Chemistry?—Our civilization rests upon chemical foundations. When primitive man first employed fire as a tool he accented the differences between man and the other animals. Yet fire is the chemical tool which made possible the Bronze Age, the Iron Age, and the Age of Machinery.

Transportation once depended upon the labor of men and animals; upon chance winds; but now the chemical power released from coal, gasoline, and oils drives steel ships along the water lanes, steel locomotives along steel rails, rubber-tired automobiles along cement roads. Without the services of chemistry the steel, vulcanized rubber, cement, gasoline, and various alloys vital to the modern automobile could not exist.

Without paper and inks the learning of the past would now be largely a matter of inaccurate oral tradition. The flashing of news across the face of the globe depends upon the chemical separation of copper from its ores and upon other chemically prepared materials. The crude "picture writing," so laboriously achieved by our primitive ancestors has become modern photography with infinite possibilities for learning and amusement, thanks to chemistry.

Think of surgery without anesthetics and antiseptics; of airships without light, strong alloys and gas or gasoline; of clothing without dyes; painting without colored pigments. We might almost as well try to build bridges and office buildings without steel and concrete; to dig tunnels and a Panama Canal without explosives.

The greatest advances in medicine are now chemical, where once they were biological. Our attack upon disease by beneficent drugs is chemical. So is the digestion of food. So are the most vital processes of animal and plant growth.

Chemistry treats of the composition and changes in composition of substances. It is also concerned with their properties and their energy relations.

We may go further and state that chemistry deals with the detection of substances, their separation from mixtures, and their preparation.

Separation of a desired substance from incidental impurities is illustrated well by the winning of gold from the sand or rock in which it occurs and by the removal of the rare gas krypton from air in which it occurs to the extent of one part in 1,000,000.

The detection of substances is managed so well by chemists that, for example, one part of poisonous mercury vapor in 20,000-000 parts of air may be recognized by the blackening of paper coated with sensitive selenious sulfide.

The preparation of desired substances is so familiar to the chemist that he makes thousands of useful compounds that "never were before on land or sea."

Problems to be solved are pressing on the chemist from every side. It is only about forty years since eminent scientists were convinced of the sure and terrible approach of a world wheat famine. Their estimates were based on the exhaustion of known fertilizer sources. The chemist accepted this challenge and indefinitely postponed the threatened famine by "fixing" the limitless nitrogen of the air, and converting it into fertilizer acceptable to plants—one of the most important achievements of modern science. We are warned that petroleum will be exhausted in much less than a century, with the result that autos will lack gasoline, ships will lack fuel oil, and modern machinery will lack lubricants. The chemist has already looked ahead to this crisis and gives good promise of meeting it.

Physics is largely a study of the various forms of energy such as light, heat, electricity, sound, mechanical energy, etc., while chemistry deals more with matter. However, each science is forced to include both matter and energy in its field. Chemistry, like physics, is universal.

Energy Transformations.—The relation between matter and energy is very close. Matter is difficult to define with exactness, but we usually consider matter as anything that has mass or weight and that occupies space. The mass of a body is the property that determines the acceleration it will acquire when acted upon by a given force.

"Energy is work, and everything which can arise from work or be converted into work" (Ostwald). Its common forms are heat, light, electricity, kinetic energy (that of moving bodies), and chemical energy. The potential energy of position of bodies might well be included in this list for the water on the brink of Niagara Falls is certainly able to do much work before it reaches the gorge below.

The free transformation of one form of energy to another is vital to our existence and welfare. Chemical energy stored up in coal may be released as heat just as truly as the chemical energy contained in our food may be converted into the motion and heat of our animal bodies. When the composition of a given portion of matter is changed energy may be released, yet, conversely, light, heat, and electrical energy may be applied to a portion of matter so as to force a change in composition. Heating limestone in the kiln changes it into lime and carbon dioxide. Light reduces the sensitive silver bromide on a photographic plate to metallic silver and bromine, and light also causes the wallpaper and the curtains to fade. A sharp blow decomposes nitroglycerine, although, to be exact, it merely starts decomposition. Infinitely more energy is released than is accounted for by the sharp blow. Electricity decomposes silver salts in solution, depositing metallic silver on objects to be plated.

The Law of the Conservation of Energy, that *in all ordinary transformations energy is neither created nor destroyed* is merely a generalized statement of a great many observations. We are coming to believe that there are some extraordinary transformations of matter into energy and energy into matter. There is strong evidence that some of the mass of the sum is lost only to reappear as radiant energy.

Substances.—A substance is a particular kind of material such as gold, sugar, common salt, or sulfur with specific properties, while a body is merely a definite portion of material such as a bottle, a kettle, a stove, or a statue. A bottle may be shaped from the mixture of substances called glass, a kettle from the substance copper, a stove from the substance iron, and a statue from the substance marble; yet the glass could be shaped into a kettle or statue, and the marble into a bottle. Evidently, then, shape and size do not identify glass, although they may well serve in classifying bottles.

The ancient Greek philosophers taught that fire, earth, air, and water were the essentials of all matter and that substances varied only in the proportions in which these four essentials were possessed.

Elements.—Substances that we can decompose into two or more simpler substances are called ***compounds***. Limestone is a compound substance because on heating in the limekiln it breaks down into quicklime and carbon dioxide. Red mercuric oxide on being heated is decomposed into the colorless gas oxygen and the metal mercury. Hence both limestone and mercuric oxide are compounds. There are more than two hundred and fifty thousand known compounds.

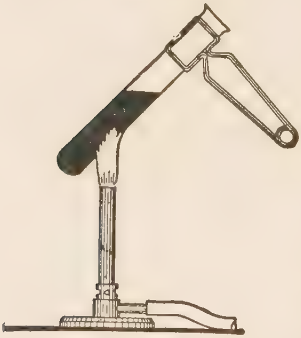

FIG. 1.—Heating mercuric oxide to obtain oxygen.

An element is a substance that cannot be decomposed into two or more substances by ordinary chemical methods. While making this flat statement we must admit that methods at present unknown may become the common methods of the future. Until 1808 quicklime or calcium oxide was called an element but in that year Sir Humphrey Davy prepared calcium and showed that it unites with oxygen of pure dry air to form quicklime. Familiar examples of elements are iron, copper, oxygen, gold, mercury, sulfur, and carbon. About ten of the elements are gases, mercury and bromine are liquids, and the rest are solids at ordinary temperatures.

At the beginning of the Christian era the scientific world knew only seven elements—gold, silver, copper, tin, lead, iron, and mercury. Up to the time of Lavoisier, 1750, only seventeen were known. In 1891 Remsen listed sixty-seven. Lavoisier called lime an element because it had not been decomposed up to his time. Now we know it is a compound of calcium and oxygen.

Rutherford bombarded many elements with the fast-moving particles constantly thrown off by the disintegration of radium and observed a slight but distinct decomposition of nitrogen, aluminum, sodium, phosphorous, boron, and fluorine.

Although now about ninety elements are known, many of them are unusual. Oxygen makes up one-half the known crust of the earth and silicon one-fourth. Fully 96 per cent of the mass of meteorites is due to iron, oxygen, magnesium and silicon. The composition of the land, ocean, and air, as we know them, is estimated to be as below:

It takes seventy-four elements to make up one per cent of the earth's crust. The great majority of chemists have never seen nor worked with all the elements; in fact some of the elements are mere curiosities with no known use. But there is always the exciting possibility that the museum specimen of today may become of invaluable service to the world tomorrow. How short a time it has been since tungsten was of little consequence and radium unknown! Tellurium is almost useless now, but who can predict its future? Neon, an inert gas which Sir William Ramsay found in the air in the proportion of one part in 80,000, had only academic interest until we recently began to employ neon lighting tubes for beacons and advertising. Its pink-orange glow is penetrating and arresting.

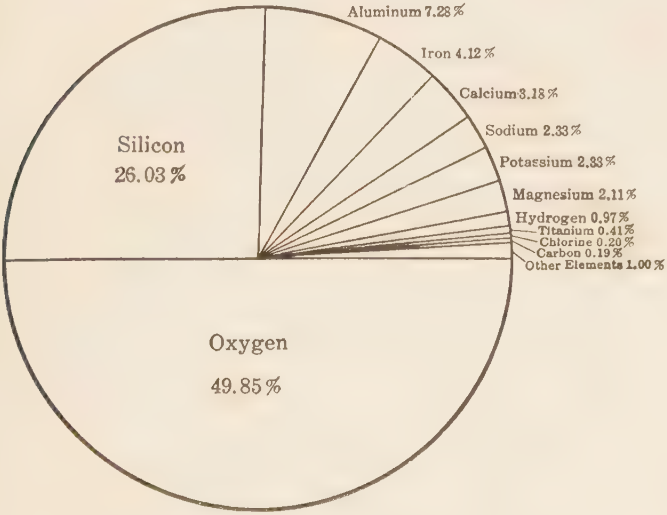

FIG. 2.—Percentage of elements in the earth's crust.

ELEMENTS OF THE HUMAN BODY

(PER CENT WEIGHT)

Oxygen	65.00	Sodium	0.15
Carbon	18.00	Magnesium	0.05
Hydrogen	10.00	Iron	0.004
Nitrogen	3.00	Iodine	0.00004
Calcium	1.50	Fluorine	a trace
Phosphorus	1.00	Silicon	a trace
Potassium	0.35	Arsenic	a trace
Sulfur	0.25		

EXERCISE 1.—Aluminum is now made from bauxite ore, yet common clay is rich in this metal. Why, then, does aluminum cost much more than iron, although more abundant in the earth's crust?

Properties.—We identify different substances by certain characteristics called properties. Bodies are recognized by such properties as size and shape although these bodies, for example, bottles and spoons, may be of wood, glass, iron, etc. But substances must be identified by other properties. We must know whether a given substance is a solid, liquid, or gas at ordinary room temperature. The temperature must also be specified, since water, for example, may be solid ice, liquid water, or gaseous steam at different temperatures.

To identify substances completely we want to know the color, odor, taste, hardness, crystalline form, melting point, boiling point, density, solubility in water or in other solvents, ability to conduct electricity, index of refraction, and other properties. We may even ask if the given substance burns in the air. The student readily recognizes sulfur as such because it is a yellow solid found in nature in rhombic crystals, melting at about 115° C., insoluble in water but soluble in carbon disulfide. If still undecided, he burns it in the air, notes the blue flame, and throws aside all doubts after one breath of the choking gas formed. In recognizing lead a student is particularly interested in its softness and its low melting point. Sugar he knows at once by its sweet taste, although indiscriminate tasting is not to be recommended. Hydrogen sulfide once smelled is never forgotten and never separated from the thought of rotton eggs. In fact we pay money for specific properties of substances. Copper would not sell for about fifteen cents a pound to the amount of over a million tons yearly if it were not such an excellent conductor of electricity. Obviously, if glass were opaque or if it dissolved readily in water, it would have no market for use as window panes.

Exercise 2.—How do you recognize copper, lead, paraffin, salt, vinegar, ammonia, water, alcohol, gold, silver, soap, gasoline?

Changes.—Changes in properties seem to be necessary to life itself. Earth, air, and water are transformed by nature's chemical processes into green grass, trees, flowers, and yet each year these beautiful new products decay and return to earth, air, and water. Iron in moist air rusts with a sharp change in properties, but the change is not hopeless, for great quantities of rusty old iron and steel are annually sent to steel mills to be converted into good steel. All of the rust is changed chemically.

When a platinum wire is highly heated only a few properties change. Instead of the usual silver white, the color changes to red as the temperature rises, yet the hot platinum differs in very few respects from cold platinum. Moreover, on cooling all of its usual properties are resumed. A physical change has taken place.

If pure white sugar is heated to a high temperature, it turns black and gives off steam. The black cinder left no longer tastes sweet nor will it dissolve in water. In fact nearly all the properties of the sugar are changed. The student cannot mix the steam and the black cinder (carbon) with any prospect of combining them into the sugar from whence they came. The change is chemical and, in this instance, hopelessly permanent. None of the resulting products have the same composition as the sugar.

A ***physical change*** is a temporary change in certain properties such as color, density, conduction of electricity, and ductility. When the original conditions are restored the original properties return. Ice may be melted and the resulting liquid water changed into steam without any change in the composition of the water. On cooling sufficiently, all of its usual properties are restored. Such changes in water are chiefly physical.

A ***chemical change*** is an abrupt and usually permanent change of certain properties with formation of new substances and is always accompanied by a gain or loss of energy. Wherever a chemical change takes place we have a chemical reaction.

It is not always easy to make a sharp distinction between chemical and physical changes. Of course when steam is cooled and condensed the original properties of the water are again observed. But what about a broken engine wheel? Restoring the fragments to their original position does not give us again a strong and useful wheel. When water is heated to nearly 2000° C. it is decomposed, to some extent, into its constituent elements, hydrogen and oxygen, yet on cooling these two elements react to form water. The change is reversible upon restoring the temperature conditions, but it must be admitted that it is a chemical change.

Lavoisier as early as 1785 believed that *in chemical reactions the mass of the system is not changed.* (Law of Conservation of Mass.) Naturally this belief came from careful weighing of the reacting materials and *all* the products. In the instance of burning wood the gaseous products as well as the ashes must be caught and weighed.

Landolt demonstrated the above law with a sealed glass tube shaped like a V. After one of the reacting substances had been introduced into one leg of the tube and the other into the second leg, the tube was sealed, cooled, accurately weighed, and then tilted so as to mix the two reagents. After restoring the original temperature the tube with its contents (a complete system) was again weighed. Within the limits of human experimental error there was no change in weight. Reaction evidently consists in rearrangement of constituent elements.

EXERCISE 3.—Give a few illustrations of physical and chemical changes.

Pure Substances and the Law of Definite Composition.[1]—*Every pure compound has a definite composition.* Water from any portion of the earth, if pure, is composed of hydrogen and oxygen in the proportion of 1 part of hydrogen to 7.94 parts of oxygen by weight. If other elements are present, they represent impurities and can readily be separated from the water. Any mixture of alcohol and water might look like water, but it would not be a pure substance. Incidentally it would not boil at 100° under 760 mm. pressure as does water, nor would it act chemically towards other substances exactly as does water. Sugar and clean white sand might be mixed very deceptively, but the analysis would show a very different composition from sugar. Such a material would not be a pure substance. If the sand were removed (How could you do it?), the remaining sugar would have the same percentage of carbon, hydrogen, and oxygen as any other specimen of pure sugar.

---

[1] Often called the *Law of Definite Proportions.*

The difference between pure compounds and mechanical mixtures is evident from this ***Law of Definite Composition.*** The proportions in any mechanical mixture may be varied considerably, as in the sand-sugar material, but if the proportions of carbon, hydrogen, and oxygen in pure sugar were changed, the substance would no longer be sugar. As a matter of fact, alcohol is composed of the same elements as sugar and can be made from it, but the percentage composition is different. Thousands of pure substances contain only these three elements, but in each case either the proportions or the arrangement of atoms are different. The formation of compounds is always attended by a pronounced energy change. Not so with mere mixtures.

A startling exception to the Law of Definite Composition was observed by Richards and by Soddy, who showed that the proportion of lead in lead chloride made from certain radioactive ores differed slightly but distinctly from the proportion of lead in common lead chloride. This exception, which is discussed later, does not change our belief in the practical validity of the law.

Mechanical separations make use of the magnet, settling, sieving, distillation, freezing, crystallization, diffusion, melting, and similar methods.

A classic illustration of the difference between a mechanical mixture and a chemical compound is found in an experiment with iron and sulfur. If very fine iron filings are mixed with flowers of sulfur, it may be shown that the sulfur still retains its own characteristic properties as does the iron, and that each may be removed by simple mechanical means. A magnet attracts the iron as if the sulfur were not present. Carbon disulfide dissolves the sulfur out of the mixture as if the iron were not present and, on filtration, a clear solution (the filtrate) is obtained. This yields the sulfur if allowed to evaporate.

If the mixture of iron and sulfur is heated in a test tube, interesting color changes are observed. Finally the mixture glows brightly, even after it is removed from the flame. Evidently heat is given off by some sort of action between the two elements. On breaking the tube a black solid is obtained which is not attracted by the magnet and from which sulfur is not dissolved by carbon disulfide. The conclusion is that neither free iron nor free sulfur is present, and that they have combined to form a compound. A reaction took place which when well started gave off considerable heat.

The experiment goes as described if the two elements are taken in a very definite proportion. If more iron than is called for by that proportion is used, some free iron is left over. If more sulfur than is called for is used, some sulfur is left over. The hard black solid obtained in the above experiment is a compound called iron sulfide. It has several properties quite different from those of iron or sulfur.

Exercise 4.—Is granite a mixture or compound? How about brass, flour, iron rust, sugar, ice cream, and whisky?

Exercise 5.—In general how could you distinguish between compounds and mixtures?

Combining Weights (Equivalent Weights).—The Law of Definite Composition created an interest in the *ratio* of the weights of elements combined in a pure compound. These combining weight ratios are easily calculated from the analysis of pure compounds. Since most elements unite directly with oxygen it is possible to learn from actual experiment what weight of each element will combine directly with a fixed weight of oxygen. These numbers may then be compared.

volume molecules : water H_2O.

Berzelius arbitrarily chose the number 100 as representing the "fixed weight" in grams, or parts of oxygen, but he might just as well have used some other number. In fact, during the century elapsed since Berzelius' time chemists have agreed that it is most convenient to assign the value eight parts (or grams) as the fixed weight of oxygen to be compared. Since eight grams of oxygen unite directly with 1.008 grams of hydrogen (to form water), this choice insures a value of at least unity for hydrogen the lightest known substance.

In the following table are listed the relative weights in which some of the elements combine with eight grams of oxygen.

Substance	Percentage Composition by Analysis		Number of Grams of the Element Uniting with 8 Grams of Oxygen
Magnesium oxide	Magnesium	60.32	12.16
	Oxygen	39.68	
Copper oxide	Copper	79.9	31.80
	Oxygen	20.1	
Water	Hydrogen	11.19	1.008
	Oxygen	88.81	
Aluminum oxide	Aluminum	52.94	9.00
	Oxygen	47.06	
Carbon dioxide	Carbon	27.27	3.00
	Oxygen	72.73	

atoms – in substance

From this table a partial list of combining (or equivalent) weights may be derived.

Oxygen	= 8.0	Hydrogen	= 1.008
Magnesium	= 12.16	Aluminum	= 9.0
Copper	= 31.8	Carbon	= 3.0

Since 1.008 grams of hydrogen are evidently equivalent in combining power (as in water) to 8 g. of oxygen, it might be conjectured that the weight of any element uniting with 1.008 g. of hydrogen would probably unite (if at all) with exactly 8 g. of oxygen. In the case of chlorine, 35.46 g. unite exactly with 1.008 g. of hydrogen, and, true to the above assumption, 35.46 g. of chlorine unite with 8 g. of oxygen.

Fluorine will not unite with oxygen but will unite with silver to form silver fluoride. The combining weight of fluorine is obtained in terms of silver which is, in turn, obtained in terms of chlorine, etc.

Oxygen	Hydrogen	Chlorine	Silver	Fluorine
8 g.	1.008 g.	35.46 g.	107.88 g.	19 g.

Exercise 6.—Predict how many grams of magnesium would combine with (be equivalent to) 35.46 grams of chlorine. How many grams of calcium, and of copper, would unite with 35.46 grams of chlorine?

[illegible]

It is evidently reasonable to state that *the combining (or equivalent) weight of any element is the number of grams of that element that combines with or displaces 8 g. of oxygen or 1.008 g. of hydrogen.*

Since there are instances where two elements combine in different proportions to form a series of compounds, we may suspect that it is possible for some elements to have at least two combining weights. The two oxides of carbon illustrate this fact.

	Oxygen	Carbon
Carbon dioxide	8 g.	3 g. (= 1 × 3 g.)
Carbon monoxide	8 g.	6 g. (= 2 × 3 g.)

The two oxides of hydrogen may also be cited.

	Hydrogen	Oxygen
Water	1.008 g.	8 g. (= 1 × 8 g.)
Hydrogen peroxide	1.008 g.	16 g. (= 2 × 8 g.)

The five oxides of nitrogen are radically different in properties, yet all contain only nitrogen and oxygen.

	Nitrogen	Oxygen
Nitrous oxide	14 g.	8 g. (= 1 × 8 g.)
Nitric oxide	14 g.	16 g. (= 2 × 8 g.)
Nitrogen trioxide	14 g.	24 g. (= 3 × 8 g.)
Nitrogen tetroxide	14 g.	32 g. (= 4 × 8 g.)
Nitrogen pentoxide	14 g.	40 g. (= 5 × 8 g.)

It is evident that the elements combine in the ratio of their combining weights or simple whole multiples of these. *The Law of Multiple Proportions* (a mere generalization) is often stated as follows: *If two or more elements form a series of compounds the different weights of one which combine with a definite weight of another stand to each other in the ratio of small whole numbers.*

32 CO_2
CO 16

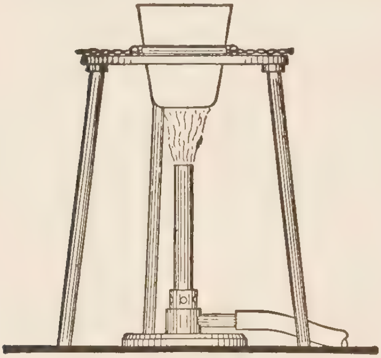

Fig. 3.—Heating magnesium to convert it into the oxide.

The combining weight of magnesium, for example, may be determined in the laboratory by heating a weighed quantity of this metal in a porcelain crucible as in Figure 3. The cover is kept on during the heating, which is gentle at first, but finally reaches the limit of the flame. After cooling, the ash, chiefly magnesium oxide with a little magnesium nitride, is moistened with a few drops of water. The nitride reacts with the water to form ammonia and magnesium hydroxide. The latter is converted into oxide on reheating. After a final weighing the gain in weight due to combination of oxygen of the air with the metal is easily calculated. By a simple proportion the number of grams of magnesium reacting with 8 g. of oxygen is found.

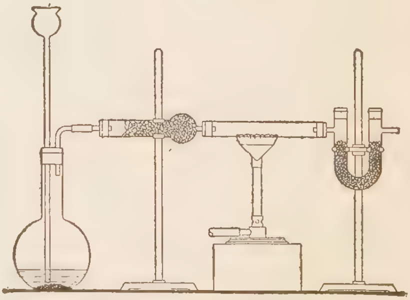

Fig. 4.—Reduction of hot copper oxide by hydrogen.

The combining weight of copper may be determined by passing air or pure oxygen through a glass tube containing a weighed amount of heated copper powder. Black copper oxide is formed. Or copper oxide may be torn apart with the aid of hot hydrogen and the loss in weight noted. For example the student may weigh out black copper oxide in a small porcelain boat and, after placing the boat in a hard-glass tube, pass dried hydrogen gas through the tube while heating (Figure 4). The hydrogen unites with all the oxygen of the copper oxide, leaving red copper. The steam formed is driven out by the steady stream of hydrogen. From the original weight of the copper oxide and the final weight of the copper one can, by simple subtraction, learn the weight of oxygen. An illustration follows:

Weight of boat + copper oxide = 4.178 g.
Weight of boat alone = 2.058 g.

Weight of copper oxide = 2.120 g.

Weight of boat + copper (after action) = 3.758 g.
Weight of boat alone = 2.058 g.

Weight of copper = 1.700 g.

Weight of copper oxide = 2.120 g.
Weight of copper alone = 1.700 g.

Weight of oxygen = 0.420 g.

Evidently 1.700 g. of copper combined with 0.420 g. of oxygen, as may be learned by subtracting the weight of the copper from the weight of copper oxide. To learn how many grams of copper would combine with exactly 8 g. of oxygen at this rate, we write a proportion.

1.70 g. copper : 0.420 g. oxygen :: x g. copper : 8 g. oxygen

Optional,

$$\frac{1.70}{0.420} = \frac{x}{8}.$$

Solving,

$$x = 32 \text{ g.}$$

Therefore the combining (or equivalent) weight of copper is 32 (approximately).

Exercise 7.—Since the oxygen and hydrogen escape as steam, could you determine by the above experiment how many grams of hydrogen combine with 8 g. of oxygen?

It is difficult to make metals unite with hydrogen, but most metals will displace hydrogen from acids. The number of grams of any metal—zinc, for example—that can take the place of one gram of hydrogen in an acid is certainly equivalent to the one gram of hydrogen, for it is combining with the rest of the compound just as did the one gram of hydrogen. For example, 32.7 g. of zinc displace 1 g. of hydrogen from acids.

Because the combining weight of many elements varies from compound to compound these weights as fundamental units are far from ideal. With the development of the conception of *atoms* as simple reacting units (following chapter) a table of *atomic weights*, invariable units of quantity, was gradually built up. These resemble combining weights and, indeed, are either the same or small multiples of their combining weights.

Element	Combining Weight	Atomic Weight
Oxygen	8.	16. (= 2 × 8)
Hydrogen	1.008	1.008 (= 1 × 1.008)
Chlorine	35.46	35.46 (= 1 × 35.46)
Copper	31.8	63.6 (= 2 × 31.8)
Carbon	3.0	12. (= 4 × 3)
Sodium	23.	23. (= 1 × 23)
Aluminum	9.	27. (= 3 × 9)

EXERCISES

8. If hydrogen reduced hot lead dioxide, PbO_2, to metallic lead, Pb, how would you represent the reaction by a balanced equation?

9. What type of change takes place when water freezes? When lard melts? When iron rusts? When a loaf of bread is scorched? When coal burns?

10. What type of change is observed when a rubber band is stretched? When a rubber band is burned?

11. Define a body, a substance, a compound, an element, a physical reaction, atomic weights, a combining weight (or equivalent weight).

12. State the Law of Definite Composition, the Law of Combining Weights, the Law of Multiple Proportions.

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CHAPTER II

THE ATOMIC THEORY

Ancient Greek Theories of Matter.—The divisibility of matter has always been familiar to man, but it remained for the early Greek philosophers, disputing without the wholesome check of laboratory experiment, to set a theoretical limit. The smallest particles of matter conceivable in their wildest flights of imagination they called *atoms*. The conception of atoms as extremely minute, compact, indivisible pellets was held by many scientists for centuries.

On the other hand Aristotle decided that all matter must be made up of at least four elements, Fire, Earth, Air, and Water, and possibly a vague fifth, or "Quintessence." His overwhelming authority dominated scientific thought for a thousand years and more. These four "elements" were really thought of as attributes or qualities of matter and were imagined as present in different substances.

Fire	the quality of Heat
Earth	the quality of Cold
Air	the quality of Dryness
Water	the quality of Moistness

The Alchemists.—The idea of varying the proportions of these qualities in matter suggested, some centuries after the time of Aristotle, the possible transmutation of one substance into another. Many secret cults, mystical writings, much self-deception and much quackery marked the development of chemistry, or *alchemy*, as it was termed from the third century to the fifteenth or even later.

The art was originally Greek, carried to Alexandria in the golden days of Egyptian learning, preserved by the Arabs, and finally carried by them into Western Europe. The continual struggle to convert base metals into gold enlisted the patronage of kings, who hired their private alchemists to replenish royal treasures. Yet in spite of the lack of order and system alchemy did carry on much knowledge into the Middle Ages.

Dalton's Atomic Theory.—The " vague atomistic theories " of ancient Greek philosophers were of little real value and were discarded by 1803. John Dalton, an English scientist, sought an explanation for the facts described by the laws of definite composition and of multiple proportion. His useful theory has been stated as follows:

1. The ultimate particles of a pure substance, simple or compound, are alike in size and weight.

2. The "simple atoms" of an elementary substance are indivisible, and can neither be created nor destroyed.

3. The "compound atoms" of a chemical compound are formed by the union of two or more elementary atoms.

4. Combination between atoms takes place in the simplest possible ratios, e.g. one atom of A with one, two, or three atoms of B.

The smallest particles of these compounds, formed by the union of two or more atoms of different elements, we call ***molecules*** The smallest particles of elements taking part in chemical reactions we call ***atoms***. A reaction, then, is merely a re-grouping of the atoms in new combinations. Two or more atoms of the same kind may unite to form molecules of an elementary substance.

This theory explains why, during a reaction between substances in a closed vessel, there is neither gain nor loss of weight (***Conservation of Mass***). All the atoms of the reacting substances are accounted for in the new substances.

It explains also the law of ***Definite Composition***. Thus if it is true that when one element unites with another the combination always takes place between a definite number of each kind of atoms, then the resulting compound must necessarily have a definite composition. For example, if two atoms of hydrogen unite with one atom of oxygen to form water, and if an oxygen atom weighs, say, sixteen times as much as a hydrogen atom, it surely follows that the percentage of oxygen and hydrogen by weight in pure water is always the same.

It also explains the law of ***Multiple Proportion***. When two atoms of hydrogen unite with *two* atoms of oxygen (instead of one) we should have a new compound quite different from water. Such a compound is known under the name of hydrogen peroxide.

The numbers called combining weights are proportionate to the masses of the atoms reacting. The fact that some elements have more than one combining number is accounted for on the supposition that atoms combine in different ratios, as do lead and oxygen.

The atomic theory has been of enormous value in the development of chemistry. For a century it served as a good working hypothesis without any absolute proof of its correctness, but recently through studies in Radioactivity we have obtained convincing evidence of the existence of atoms and molecules and have even counted and weighed them. Millikan reports the number of molecules in a cubic centimeter of any gas under standard conditions as 2.71 x 10^{19}, a value closely confirmed by several different methods.

Molecules are so small that if we empty one liter of water into the ocean, with thorough mixing, and then dip out one liter, we will recapture 2220 of the original molecules of water added to the ocean. A row of 40,000,000 molecules in contact would measure one inch.

The Modern Atomic Theory.—Dalton's atomic theory did not explain why some elements react with each other and others do not, what forces hold atoms together in molecules. and how the constituent atoms are arranged.

About 1878 Sir William Crookes discovered that high-vacuum tubes conduct electricity, at high voltage (Figure 5). Sealed-in wires at *A* and *C* support the anode and cathode. No matter what the gas, nor what material the cathode, peculiar radiations called "cathode rays" emanate from the cathode and cause a greenish fluorescence where they hit the glass wall of the tube. For that matter, they may heat to incandescence a piece of metal such as copper or tungsten interposed in their path. When a cathode tube is placed between two metal plates, one carrying a heavy positive charge and the other a heavy negative charge, the rays are deflected toward the positive plate. The conclusion is that the cathode rays are a stream of negatively charged particles. And since these same particles are thrown off from the cathode (or the gas?) no matter what the cathode or gas, they must be constituent parts of all atoms.

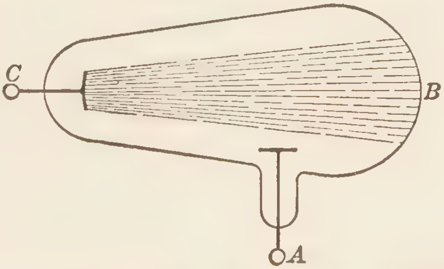

Fig. 5. — Crookes tube, showing cathode rays.

The great English physicist, J. J. Thomson, discovered in 1897 that these negatively charged particles (at first called corpuscles and later *electrons*) exist in the atoms of all elements. He even determined that they have a mass of only 1/1845 of the mass of the hydrogen atom, the lightest of all atoms. Furthermore, the element radium was found to throw off not only electrons at high velocities, but positively charged particles. This "radioactive disintegration," limited to very few elements, is a spontaneous process not under our control in any way.

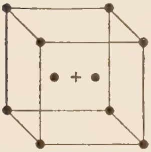

FIG 6.—The neon atom (purely diagrammatic). The nucleus is represented by +.

Out of such work since 1897, including Rutherford's discovery of the *proton* in 1911, has come the modern conception of atomic structure, admittedly incomplete, but based upon unquestioned facts. We now feel certain that the ordinary neutral atom is a miniature solar system with a compact central nucleus made up of electrons (negative charges of electricity) and a larger number of protons (positive charges of electricity), and enough more planetary electrons to balance electrically the excess of protons in the nucleus. So small are these two fundamental units, electrons and protons, that the atom is mostly space. So too, is the solar system.

In all probability the planetary electrons rotate at great velocities around the nucleus, although many chemists believe that they merely vibrate back and forth across the general center of the atom.

The simplest atom is hydrogen, made up of a single proton and a single electron. The most complex atom is uranium, with 238 protons and 238 electrons. Since the hydrogen atom weighs 1.008 and the electron mass is only 1/1845 of the hydrogen mass, it is evident that the proton has a mass of approximately one. In other words, the mass of electrons is negligible, and practically all the weight, or mass, of an element is concentrated in the nucleus, a relatively very minute fraction in volume of the entire atom.

Although the electrons (negative), are attracted by the nuclear protons (positive), some of the outer planetary electrons are known to escape to other atoms. Curiously enough some of the most active atoms, like those of the metals potassium and sodium, have a very great tendency to throw off outer electrons, while some of the most active non-metallic atoms like those of chlorine and fluorine exhibit a reluctance to throw off electrons, but show an eagerness to take on electrons. Now we understand why two such active elements as potassium and sodium refuse to react with each other. Each type of atom is attempting to do the same thing—throw off an electron. On the other hand, sodium reacts with chlorine, because the chlorine atom eagerly takes on the electron that the sodium atom is so willing to discard. Chemical reaction takes place and a molecule of sodium chloride, common salt, is found. The loss of a negative electron from an electrically neutral sodium atom leaves an excess of one proton, or positive charge, on that atom, while the gain of an electron by a neutral chlorine atom confers a negative charge on that atom. Consequently the two oppositely charged atoms are held together in the molecule of salt by electric attraction. (In some types of reaction electrons in pairs are shared by atoms.)

The atoms of the inert elements like helium, neon, and argon are so stable that they neither gain nor lose planetary electrons, consequently they never react with anything, form no compounds at all.

The radio has made everybody familiar with electrons. Glowing hot wires emit electrons, in fact we now know that a current of electricity coursing through a wire is merely a stream of electrons passing from atom to atom of the wire.

In the nineteenth century the prevailing idea seemed to be that atoms are indivisible, and extremely hard and indestructible. The idea was expressed in an interesting way by Newton:

"It seems probable to me, that God in the beginning formed matter in solid, massy, hard, impenetrable, movable particles, of such sizes and figures, and with such other properties, and in such proportion to space, as most conducive to the end for which He formed them; and that these primitive particles, being solids, are incomparably harder than any porous body, compounded of them, even so very hard as never to wear or break in pieces; no ordinary power being able to divide what God Himself made one in the first creation."

EXERCISES

1. State Dalton's Atomic Theory.
2. Define an atom, a molecule, an electron, a proton, and nucleus.
3. What changes have been made in Dalton's Atomic Theory to bring it up to date?

4. Why should potassium and chlorine atoms react with each other while potassium and sodium do not? For that matter sodium reacts with chlorine.

5. Why is there no gain or loss in weight during a chemical reaction?

6. What evidence have we that negatively charged particles are among the constituents of all atoms?

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CHAPTER III

SYMBOLS, FORMULAS, AND EQUATIONS

Symbols and Formulas.—Up to the time of Berzelius, about a century ago, chemists used strange symbols for the elements. The moon ☾ represented silver, △ was the symbol for water, ♀ stood for copper, and 🜍 for sulfur. But these were supplanted by Berzelius' suggestion that one or two significant letters of the name of the element be used. Thus the symbol for carbon is C, for copper Cu, for chlorine Cl, for calcium Ca, and for cobalt Co. To avoid confusion Ag (from the Latin *argentum*) was taken as the symbol for silver because S had already been selected for sulfur and Si for silicon. Fe for iron is taken from the Latin *ferrum*, Na for sodium from *natrium*, Pb for lead from *plumbum*, and K for potassium from *kalium*. According to our present conception symbols stand not only for the elements but for definite parts by weight of the elements. For example, H represents a single atom of hydrogen and it may also mean the atomic weight in grams, that is, one gram. O means either a single atom of oxygen or 16 g. of oxygen.

To represent the formula of a compound we simply join the symbols of the constituent elements together and attach small sub-figures to represent the actual numbers of atoms in each molecule. H_2O as a formula for water tells us that two atoms of hydrogen and one atom of oxygen make up a single molecule of water. The weight of the whole molecule, 18.016 is of course the sum of the weights of all the atoms in it. The formula O_2 for the substance oxygen tells us that there are two oxygen atoms in each molecule with a molecular weight of $2 \times 16 = 32$. H_2SO_4, as a formula for sulfuric acid, tells us that a molecule of the acid contains two atoms of hydrogen, one of sulfur and four of oxygen. The formula weight is 98.016 g.

TOMIC WEIGHTS	MOLECULAR WEIGHTS
H = 1.008	2H = 2.016
S = 32	S = 32
O = 16	4O = 64
	H_2SO_4 = 98.016

Equations.—With the use of symbols and formulas we can now represent chemical changes (reactions) very simply and clearly. For example, the equation [1]

$$CuO + H_2 \longrightarrow H_2O + Cu$$

tells us that one molecular weight of copper oxide reacts with one molecular weight of hydrogen to form one molecular weight of water and one of copper. The weight of one molecule of CuO is obviously the sum of the weights of all the atoms in it. $Cu = 63.57$ and $O = 16$. Therefore $CuO = 79.57$. The weight of $H_2 = 2.016$; of $H_2O = 2.016 + 16$, or 18.016; and of $Cu = 63.57$.

It is a very useful practice to consider these weights as expressed in grams. Of course the relative values are just the same whether expressed in the minute units of atomic weights, or grams, or tons. Expressed in grams we should read the equation thus:

79.57 g. copper oxide + 2.016 g. hydrogen react to form
18.016 g. water + 63.57 g. copper.

These so-called equations name the reacting substances and their products. "Balancing the equations" consists in prefixing such numbers before the molecular formulas as indicate the relative number of molecules concerned. Suppose the student knows by *laboratory observation* that hydrogen reacts with hot iron oxide to form iron and steam. He would represent this reaction tentatively by merely writing down the formula thus:

$$H_2 + Fe_3O_4 \longrightarrow Fe + H_2O \text{ (trial)}$$

but not *all* the atoms in the reacting substances are found in the products. After all, such a reaction is merely a regrouping of the elements in new combinations, so the student must account for all the atoms. There must be an *equal* number of H atoms on both sides, of Fe atoms, and of O atoms also. So the student begins with the most intricate formula and decides to try *one* molecule of Fe_3O_4. We do not prefix "1" to molecules; it is understood if no number is given. As a result of deciding to try balancing with one Fe_3O_4, we must account for three atoms of Fe on the right-hand side of the equation. Making this change, the equation will improve:

$$H_2 + Fe_3O_4 \longrightarrow 3\ Fe + H_2O \text{ (trial).}$$

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[1] It used to be the universal custom to represent such a reaction thus: $CuO + 2H = H_2O + Cu$, hence the name "equation."

It is evident that the four oxygen atoms in the Fe_3O_4 molecule are not all found in a single molecule of H_2O. It must require 4 H_2O to dispose of them. So another improvement is made:

$$H_2 + Fe_3O_4 \longrightarrow 3\ Fe + 4\ H_2O \text{ (trial).}$$

But to write 4 H_2O on the right side requires that we place 8 atoms of hydrogen on the left or there will be no equality:

$$4\ H_2 + Fe_3O_4 \longrightarrow 3\ Fe + 4\ H_2O \text{ (balanced).}$$

Now every atom is accounted for on both sides and no violence has been done to the inner structure of any compound nor has anything been represented that was not produced in the laboratory. The equation is, therefore, properly "balanced."

A chemical equation, then, must represent the reacting substances, the products formed and the relative weights involved. It does not, however, name the conditions necessary—temperature, etc.—to cause the reaction to take place, nor does it tell how rapidly it occurs nor to what extent the reaction occurs.

Calculation of Percentage Composition of Compounds from Formulas.—If the correct formula for black iron oxide is Fe_3O_4 it is a simple matter to calculate the percentage or iron, for example. From the formula we learn that the molecular weight is the sum of three times the atomic weight of iron (3 × 55.84) plus four times the atomic weight of oxygen (4 × 16), or a total weight of 231.52. The iron fraction is evidently $\frac{167.52}{231.52} = 0.7236$ = 72.36 per cent of the oxide.

$\frac{32}{98} \times 100 =$

✓

Determination of Formula from Analysis.—Suppose analysis showed a compound to contain 27.06 per cent of sodium, 16.47 per cent of nitrogen, and 56.47 per cent of oxygen. What is the formula of the compound?

In 100 g. of Compound	Atomic Weights in Grams	Number of Gram Atomic Weights of Each Element in 100 g. of Compound
27.06 g. sodium	Na = 23 g.	27.06 ÷ 23 = 1.176 sodium
16.47 g. nitrogen	N = 14 g.	16.47 ÷ 14 = 1.176 nitrogen
56.47 g. oxygen	O = 16 g.	56.47 ÷ 16 = 3.528 oxygen

This ratio between the number of gram atomic weights of the three elements present, 1.176 : 1.176 : 3.528, may be written

1 : 1 : 3. Hence there is in each molecule one atom of sodium, one atom of nitrogen and three atoms of oxygen, and the formula is $NaNO_3$. Of course this ratio would hold if the molecule were two or three times as heavy, but it is best to accept the simplest formula. Later we shall learn how to determine the weight of each molecule and to apply that knowledge to the determination of formulas.

EXERCISES

1. A certain compound contains, by analysis, 29.40 per cent of calcium (Ca), 23.56 per cent of sulfur (S), and 47.04 per cent of oxygen. What is its formula?

✓ 2. Define symbol, formula, equation.

3. From the percentage composition alone could you tell whether H_2SO_4 or $H_4S_2O_8$ was the correct formula for sulfuric acid?

4. Derive the formula of a compound containing 25.57 per cent magnesium and 74.43 per cent chlorine.

✓ 5. What per cent of lead is found in pure red lead, Pb_3O_4?

Multiple Proportions

CHAPTER IV

OXYGEN AND OZONE

OXYGEN

History.—The history of modern chemistry begins with the discovery of oxygen, the most important element. In 1774 Priestley, an English clergyman, heated a number of different substances resting on the mercury in inverted glass tubes. The source of heat was the sun's rays concentrated by a lens a foot in diameter. On heating red mercuric oxide a gas was evolved in which a splinter burned far more brilliantly than in air. Furthermore, a mouse became much more active in this gas than in air. Priestley named the gas "dephlogisticated air." It was produced from the mercuric oxide as represented by the equation:

$$2\,HgO \rightarrow 2\,Hg + O_2.$$

A year earlier Scheele, a brilliant chemist and drug clerk in Sweden, obtained oxygen by heating manganese dioxide, potassium nitrate and five other substances. Priestley published his results first, but both men deserve credit as independent discoverers.

FIG. 7. — Joseph Priestley.

NOTE: Priestley's interests included the fields of theology and government, in both of which he was too radical to suit all of his neighbors. At one time a mob attacked his house and threw his household goods into the street. In 1794 he moved to America, where he wrote and worked in his laboratory. In fact, he discovered carbon monoxide gas in this country. Although chemistry was a side interest, Priestley did invaluable work in that field, as evidenced by his discovery of oxygen, ammonia, hydrogen sulfide, nitric oxide, nitrous oxide, and sulfur dioxide. Of course some of these gases had been made before, but Priestley prepared them and recognized them as definite substances.

Lavoisier, a celebrated Frenchman, sometimes called the "father of modern chemistry," at once applied himself to a systematic study of the new substance, and by a convincing experiment showed its relation to air. He heated mercury in a retort (Fig. 8) for twelve days and then observed a red powder formed on the surface of the mercury. The end of the retort dipped under a jar in a larger dish of mercury, so the volume of the air in the retort was definitely known. During the heating this volume decreased one fifth and the gas left in the retort extinguished a burning splinter. On heating the red powder to a still higher temperature a volume of gas was given off exactly equal to the loss in volume of the retort air. Moreover this evolved gas possessed all the properties of Priestley's "dephlogisticated air." Lavoisier named it "oxygen," from the Greek word for "acid-producer," because he thought it was contained in all acids. In this he was mistaken, but he was right in his conclusion that oxygen is an essential part of air.

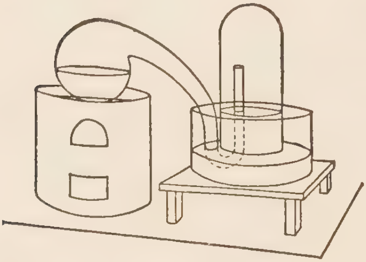

Fig. 8.—Lavoisier's experiment.

Lavoisier's experiment cleared up the current uncertain ideas of combustion and rusting, for he had calcined or rusted mercury, showing that it united with oxygen from the air to form an ash, mercuric oxide.

Exercise 1.—From some good history of chemistry (Moore, published by McGraw-Hill Co., is excellent) learn later incidents in the lives of Priestley and of Lavoisier.

Occurrence.—Oxygen makes up one-half of all matter that we know. Two-thirds of the human body is combined oxygen. Water contains 89 per cent, ordinary clay, sand, limestone and granite about 50 per cent. One-fifth of the air is oxygen, the other four-fifths nitrogen. This is the only occurrence of free oxygen. Elsewhere it is found in compounds.

Preparation.—1. The most natural source of oxygen is the air where it occurs free but mixed with nitrogen, from which it is not easily separated. The separation is accomplished by liquefying air and then allowing it to evaporate. The more volatile nitrogen escapes first, leaving the oxygen, which is usually stored in strong steel cylinders at 100 atmospheres pressure. The gas thus obtained naturally contains a little nitrogen, which does no harm for commercial uses. This modern process is now the only commercial method used on a large scale. The nitrogen also has a ready market.

One ton of coal furnishes the energy required to separate one ton of oxygen from four tons of nitrogen by the liquefaction process.

2. The electrolysis of water releases hydrogen at the cathode and oxygen at the anode. This process is used commercially to some extent because the product is very pure and because there is a good demand for the hydrogen. The cost is too great for it to compete with the liquid air process as a source of oxygen.

3. The laboratory methods, where convenience is more important than cheapness, in most cases consist in heating oxygen compounds. It is possible to follow Priestley and heat mercuric oxide:

$$2\,HgO \longrightarrow 2\,Hg + O_2.$$

The mercury is volatilized and condenses in a mirror or in drops on the cooler parts of the tube.

We may emulate Scheele and heat potassium nitrate:

$$2\,KNO_3 \longrightarrow 2\,KNO_2 + O_2.$$

Only a third of the oxygen is driven off and potassium nitrite remains.

Manganese dioxide on being heated very hot gives off only part of its oxygen:

$$3\,MnO_2 \longrightarrow Mn_3O_4 + O_2.$$

Barium dioxide releases just half its oxygen when sufficiently heated:

$$2\,BaO_2 \longrightarrow 2\,BaO + O_2.$$

In fact this was the basis of the Brin process, once the chief commercial method. Barium oxide was heated in the air at 500° C.:

$$2\,BaO + O_2 \longrightarrow 2\,BaO_2.$$

At this temperature the monoxide united with more oxygen to form the dioxide, although at 800° C. and higher the BaO_2 could be decomposed, reversing the action. By the clever device of lowering the pressure considerably and keeping the temperature constant at 700° C. the barium dioxide released half its oxygen.

The barium oxide, on increasing the pressure of air, again became the dioxide at the same temperature and the process was repeated *ad infinitum.*

Potassium chlorate melts at 351° C. and at about 400° C. releases oxygen:[1]

$$2\ KClO_3 \longrightarrow 2\ KCl + 3\ O_2.$$

If into a test tube partly filled with melted potassium chlorate which is giving off very little oxygen we drop a mere pinch of powdered manganese dioxide, there is at once an enormous increase in the rate of evolution of the gas. Potassium chlorate alone does not give off oxygen much below 400° C., yet in the presence of manganese dioxide the gas is rapidly released at 200° C. This is the basis of the usual laboratory method. No exact amount of manganese dioxide is needed. About one fourth as much as the weight of the potassium chlorate is satisfactory. The manganese dioxide aids the reaction and is called a "catalyst" (see Index). In Fig. 9 is represented the usual laboratory method of preparing oxygen in quantity. The oxygen evolved from the heated mixture of potassium chlorate and manganese dioxide is collected by displacement of water, in which it is but slightly soluble. Iron oxide, Fe_2O_3, is even more efficient than manganese dioxide.

$lO_3 + MnO_2$

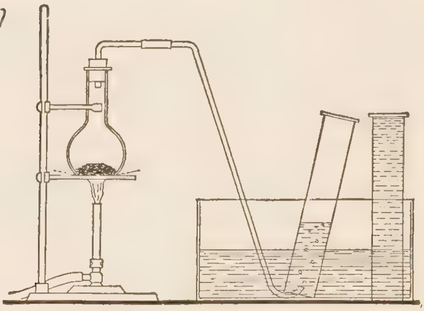

FIG. 9.—Preparations of oxygen from heated potassium chlorate and manganese dioxide.

4. Sodium peroxide (made by heating sodium in air) reacts with water to form oxygen and sodium hydroxide:

$$2\ Na_2O_2 + 2\ H_2O \longrightarrow 4\ NaOH + O_2.$$

This is expensive but very convenient, as the water may be allowed to drop slowly from a dropping funnel on the peroxide, releasing oxygen as needed.

---

[1] In reality $KClO_4$ is first formed and this at higher temperatures gives up all its oxygen.

The oxides of the least active or "noble" metals, mercury, silver, gold, and platinum, are readily decomposed on heating, while one of two of the oxides of chlorine may be decomposed explosively. The oxides and even the peroxides of sodium and potassium withstand extremely high temperatures. The higher oxides of some metals such as those of lead, manganese and barium give off part of their oxygen and yield a lower oxide when heated to sufficiently high temperatures.

Physical Properties.—It is important to have a record of the physical and chemical properties of the elements and compounds, but the student is not asked to burden his memory beyond reason.

Oxygen is a colorless, odorless, tasteless gas which is 1.105 times as heavy as air. One liter weighs 1.429 g. measured at 0° C. and a barometric pressure of 760 mm. It may be liquefied at and below −118° C., but no pressure is great enough to compress it to a liquid above −118° which may then be called its *critical temperature.* At this critical temperature 50 atmospheres pressure are required to liquefy oxygen; hence this is the *critical pressure.*

Liquid oxygen is light blue, boiling at −182.5° under atmospheric pressure. It is attracted to a magnet but far less strongly than is a bar of iron. Dewar froze oxygen to a pale blue, snowlike solid, melting at −227°.

Oxygen is slightly soluble in water. At 20° and 760 mm. pressure 100 cc. of water dissolves 3 cc. of oxygen. Curiously enough it dissolves in molten silver, 10 cc. in 100 cc. of the silver.

Chemical Properties.—Oxygen is only moderately active chemically at ordinary temperatures, but at elevated temperatures it unites with nearly every element. It is true that sodium rapidly oxidizes at room temperature but iron rusts slowly and carbon is attacked very slightly indeed.

If the metal sodium is heated and then placed in a jar of oxygen, it burns brilliantly with a yellow flame. The only possible reaction is the direct combination of the two elements forming a sodium oxide or, under these conditions, sodium peroxide:

$$2\,\mathrm{Na} + \mathrm{O_2} \longrightarrow \mathrm{Na_2O_2}.$$

Calcium burns almost as brilliantly, forming ordinary quicklime or calcium oxide:

$$2\,\mathrm{Ca} + \mathrm{O_2} \longrightarrow 2\,\mathrm{CaO}.$$

Sulfur, first ignited with a flame, also burns with far greater vigor in oxygen than in air, forming sulfur dioxide:

$$S + O_2 \longrightarrow SO_2.$$

Red phosphorus burns with a dazzling flame and formation of dense white smoke of phosphorus pentoxide.

$$4\ P + 5\ O_2 \longrightarrow 2\ P_2O_5.$$

The experiment with carbon is best performed with a stick of charcoal, which can be held in the forceps. After igniting it in the Bunsen flame, it is thrust into a jar of oxygen, where, instead of merely glowing, it bursts into flame. Pure carbon burns with a pale blue flame:

$$C + O_2 \longrightarrow CO_2.$$

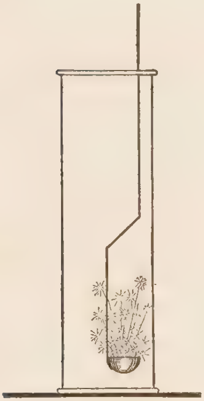

FIG. 10.—Burning iron in oxygen.

It seems incredible, but iron in the form of steel wool or picture wire will burn in oxygen if first heated red hot. It may be necessary to dip the end of the wire into sulfur as a sort of match head. Dazzling sparks (Fig. 10) fly in all directions, and drops of molten iron often break the glass bottles. Water in the jar may save the glass:

$$3\ Fe + 2\ O_2 \longrightarrow Fe_3O_4.$$

After these oxides have been formed, a little pure water is added to each jar which is then closed and shaken.

A small piece of blue litmus paper and one of red are dropped into each jar. The water on the sodium oxide turns red litmus blue, as does the calcium oxide water. Both waters feel soapy to the touch. The sulfur dioxide water turns blue litmus red as does the carbon dioxide water. The effect of the iron oxide water is too slight to be detected. These oxides have reacted with water in two ways, some to form ***bases*** which turn red litmus blue and some to form ***acids*** which turn blue litmus red. Elements whose oxides react with water to form bases are called ***metals*** and elements whose oxides react with water to form acids are called ***non-metals***. (These oxides are known as the ***anhydrides*** of bases and of acids.)

$$
\begin{aligned}
2\,Na_2O_2 + 2\,H_2O &\longrightarrow 4\,NaOH + O_2,\\
CaO + H_2O &\longrightarrow Ca(OH)_2,\\
SO_2 + H_2O &\longrightarrow H_2SO_3,\\
CO_2 + H_2O &\longrightarrow H_2CO_3,\\
P_2O_5 + 3\,H_2O &\longrightarrow 2\,H_3PO_4.
\end{aligned}
$$

The products above are called sodium hydroxide, calcium hydroxide, sulfurous acid, carbonic acid, and phosphoric acid respectively. The definition of ***acids*** will be given later, but we know them as sour substances that in water solution turn litmus red, attack some metals, and neutralize the properties of bases. We know ***bases*** as substances that in water solution feel soapy, turn litmus blue, and neutralize the properties of acids.

Metals (iron, copper, gold, nickel, and lead, for example) show such physical properties as good conductivity for heat and electricity, malleability, ductility, and luster. Non-metals (sulfur, carbon, chlorine, arsenic, and nitrogen, for example) in general do not exhibit these properties.

Oxides.—An oxide is a compound of oxygen with one other element. Water is an oxide of hydrogen. Potassium chlorate is not an oxide, for it contains more than two elements. Most oxides can be made by direct combination of oxygen with one other element, but a few elements like gold and platinum must be led into such union by indirect methods. Many oxides are made conveniently by heating carbonates, nitrates, and hydroxides. Quicklime is an example:

$$CaCO_3 \longrightarrow CaO + CO_2.$$

EXERCISE 2.—Air is a mixture of nitrogen and oxygen. When nitrogen unites with all the oxygen it can take on directly the product is a poisonous, corrosive reddish-brown gas. Now have you any reason to think that the reaction

$$N_2 + 2O_2 \rightarrow 2NO_2$$

occurs when air is moderately heated? We may ask this question again when nitrogen is studied.

Combustion.—When substances react heat is usually (but not always) liberated. If the reaction becomes so vigorous that light is also produced, it is called combustion. As a rule this term is applied to a union of oxygen with other substances, but many other reactions produce light. The burning of fuel in a furnace is a common example of combustion. Sodium and magnesium burn almost as brilliantly in carbon dioxide gas as in air, forming oxides and free carbon in each case. A jet of chlorine gas burns with a flame in an atmosphere of hydrogen gas, but a jet of hydrogen also burns in an atmosphere of chlorine.

$$H_2 + Cl_2 \longrightarrow 2\,HCl.$$

We sometimes speak of the ***kindling temperature*** as the temperature at which a given substance in contact with air bursts into flame. This is not a very definite temperature, however, as it may vary with the relative amount of surface of the substance, with the pressure of the air, and with the presence of other substances (see catalysis) that aid reactions. For example, iron can be made in a powder so fine that on exposure to the air it bursts into flame. White phosphorus (dangerous to handle!) ignites at 35° C. and carbon disulfide at 150° C. Many substances will not burn in oxygen or in air, but that may be because they already contain all the oxygen they can hold.

Phlogiston.—Becher, and later Stahl (1723), sought to explain combustion by assuming the escape of a sort of volatile spirit called phlogiston! Indeed the upward rush of flame gives some such impression. The ash of wood no longer burned because it had lost all of its phlogiston. A splinter ceased to burn in a limited volume of air because the air became filled with phlogiston and could take on no more. Combustible substances were those that contained phlogiston and their burning was merely the escape of this mysterious spirit.

Lavoisier's famous experiment (1777) described on page 26 sounded the death knell of the phlogiston theory. This experiment showed that the increase in weight which occurs during oxidation is equal to the weight of oxygen absorbed from the air.

Lavoisier in 1774 heated a weighed amount of tin in a weighed and closed flask containing air. After a few days the tin was converted into a white powder. The flask and contents had not changed in weight. (Note Law of Conservation of Matter.) Upon opening the flask air rushed in and increased the weight of the flask and contents by a definite amount. The white tin powder was removed and weighed. Its increase in weight over the original tin nearly equalled the weight of the air rushing into the flask.

Exercise 3.—Why does the ash of wood or coal weigh less than the original fuel while the ash of heated metals weighs more?

In Fig. 11 is represented a candle placed directly under an open tube filled with sticks of sodium hydroxide, all balanced by weights on the other pan of the balance. When the candle is lighted the pan on the left sinks. The increase in weight is due to the fact that oxygen of the air unites with the wax of the candle and to the additional fact that the gaseous products of combustion are caught by the sodium hydroxide. A magnet holding iron filings may be hung from the left end of the balance, and counterpoised by weights on the pan on the right. If now, the magnet and filings are heated with a gas flame the formation of an iron oxide is indicated by the increase in weight.

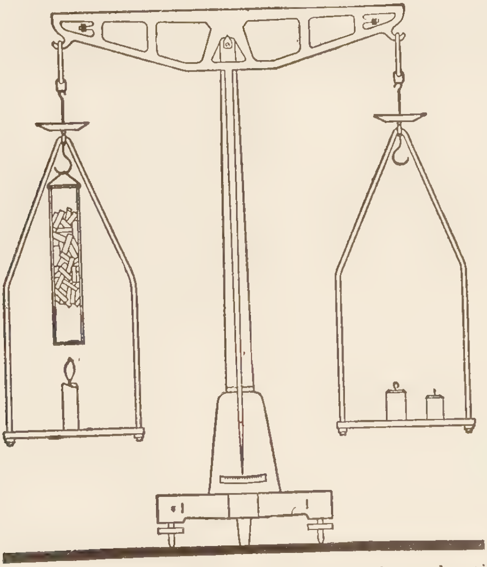

FIG. 11.—Weighing all the products of combustion.

Heat of Combustion.—Reactions accompanied by the evolution of heat are *exothermic,* and those that require the application of external heat to sustain them are *endothermic.* To measure this heat we use the calorie as a unit. A *calorie* is the amount of heat required to raise the temperature of one gram of water one degree (at 15° C.). The large calorie (Cal.) is one thousand times as great.

The *heat of combustion* of any pure substance is the number of calories liberated when the formula weight (molecular weight in grams) is burned. For example, a molecule of carbon monoxide weighs 28, hence its formula weight is 28 g. When 28 g. of this gas burns it liberates 68,000 calories and becomes carbon dioxide.

Of course the heat of combustion of hydrogen is the same as the heat of formation of water. It is also obvious that substances with the highest heat of formation must be the hardest to decompose by application of external energy. The amount of heat required to decompose a given weight of a compound into its constituents is equal to the amount of heat given off when the same weight of the compound is formed from its elements. When enough hydrogen is burned in air or oxygen to form 18.016 g. of water 68,340 cal. of heat are evolved and exactly this much energy as heat or electricity is required to decompose 18.016 g. of water into hydrogen and oxygen.

The following table gives the heat of combustion of several substances:

Substance	Formula Weight	Heat of Combustion
Carbon	$C = 12$ g.	96,960 calories
Sulfur	$S = 32$ g.	70,940 calories
Hydrogen	$H_2 = 2$ g.	68,360 calories
Carbon monoxide	$CO = 28$ g.	68,000 calories
Methane	$CH_4 = 16$ g.	211,900 calories

Exercise 4.—How much heat is liberated when 136 g. of sulfur burns? When 24 g. of carbon burns to CO_2?

A table of heats of formation of compounds from elements is a little different although of course the heat of formation of carbon dioxide as 94,400 calories, exactly the same as the heat of combustion of carbon.

Substance	Formula Weight	Heat of Formation
Aluminum chloride	$AlCl_3 = 133.35$ g.	166,800 calories
Sodium chloride	$NaCl = 58.45$ g.	98,360 calories
Calcium oxide	$CaO = 56$ g.	151,700 calories
Carbon dioxide	$CO_2 = 44$ g.	94,400 calories
Carbon monoxide	$CO = 28$ g.	26,400 calories
Hydrogen chloride	$HCl = 36.47$ g.	22,000 calories
Hydrogen sulfide	$H_2S = 34.08$ g.	5,260 calories

Engineers quite commonly refer to British Thermal Units, B. T. U., instead of calories. This B. T. U. is the amount of heat required to raise one pound of water 1° F. Since 1 lb. = 453 g. and 1° F. = $\frac{5}{9}$ of 1° C., it is evident that 1 B. T. U. = 252 calories. Very good soft coal may yield 15,000 B. T. U. per pound of dry fuel.

Exercise 5.—A ton of coal with a B. T. U. value of 14,560 per pound will raise the temperature of how many liters of water 40°?

Exercise 6.—Calculate the number of B. T. U. obtained by burning one pound of sulfur.

The *bomb calorimeter* is the apparatus in which we burn solids to measure their heat of combustion. This apparatus consists of a strong metallic *bomb,* gas-tight. A weighed amount of a solid to be burned is placed in the bomb, which is filled with oxygen under high pressure (to secure better combustion). The bomb is surrounded by a known amount of water contained in a vessel well insulated against heat loss.

A wire is heated by a current of electricity so as to ignite the substance. From the weight of water and its rise in temperature as well as similar data for the calorimeter itself we can accurately compute the total number of calories evolved.

An exothermic reaction frequently continues of its own accord when once started, but an endothermic reaction continues only when forced to do so by use of energy from external sources.

Oxidation.—The union of oxygen with a substance is called oxidation. (Later we shall find some other reactions also included under that term.) Oxidation may be so slow that no light is evolved and very little if any rise in temperature noticed. As a matter of fact when a gram of any substance is oxidized slowly exactly the same quantity of heat is liberated as during violent burning. In slow oxidation heat is usually conducted away so rapidly that a rise in temperature is not noticed. The rusting (slow oxidation) or burning of metals (rapid oxidation) is illustrated by the following equation:

$$2\,Mg + O_2 \longrightarrow 2\,MgO.$$

The change from "hard" cider to vinegar is brought about by the union of alcohol of the cider with oxygen of the air to form acetic acid. The "mother of vinegar" is an organism that aids this reaction.

The animal body is a wonderful apparatus for the oxidation of food. The oxygen of the air meets the blood in the lungs and combines with the bluish hemoglobin of venous blood to form red oxyhemoglobin of arterial blood. This oxyhemoglobin is taken through the smallest capillaries and gives its oxygen to the worn-out tissues of the body, burning them into carbon dioxide and water for the greater part. Carbon dioxide is exhaled from the lungs. The heat of this oxidation maintains the animal temperature and is approximately equal to the heat evolved when the same food is burned rapidly in a calorimeter. In other words the animal's body is both furnace and engine for the conversion of the chemical energy of food into heat and motion.

It is interesting to note that while one kilogram of bees requires 17,336 cc. of oxygen per hour in summer, one kilogram of chickens requires 740 cc., and each kilogram of man requires 233 cc., one kilogram of frogs requires only 70 cc. of oxygen per hour.

The "drying" of paint is not the loss of water but the oxidation of linseed oil to form a tough solid that is no longer sticky.

Exercise 7.—The Eskimos eat more fat than we do. What do you assume about the relative fuel values of fat and your own usual diet?

Spontaneous Combustion.—If the heat from a slow oxidation is not conducted away fast enough, it may accumulate, finally bringing the temperature of the substance to the ignition point. This is *spontaneous combustion.* Coal is oxidized on storing and a loss of several per cent occurs. Usually the circulation of air between the lumps is sufficient to conduct this heat away, but large heaps of poor coal containing a good deal of fine material sometimes rise in temperature to actual combustion. Such fires are difficult to put out and the aggregate loss is enormous, fully $20,000,000 annually in the United States. Some air circulation, but not too much, is necessary to start combustion.

Waste rags soaked in oils, like linseed, which oxidize readily, are very likely to ignite spontaneously. It is safer to dispose of such oily waste or to keep it in closed tin cans. Petroleum lubricating oils do not offer this hazard.

Uses of Oxygen.—Oxygen is a most useful element. Essential to animal life in burning out waste tissue and furnishing heat, beneficent in its disposal of sewage and other waste matters that would otherwise be a nuisance and a menace to health, vital in developing heat, light, and power from fuel—it is, in short, the central element. Oxygen, compressed in steel cylinders, is used for the oxyhydrogen (or oxyacetylene) torch. This is a burner by which hydrogen or acetylene is burned in pure oxygen instead of in air. The extremely hot flame produced cuts through iron (by melting and burning the iron) like a knife. The transportation of scrap iron occurring in such inconvenient forms as bridges, boilers, etc., is tremendously aided by cutting it into smaller sections with the oxyacetylene torch. Again the localized high temperatures are convenient in welding. Unfortunately the oxyacetylene flame has been of great help to burglars in opening safes. Over three billion cubic feet of compressed oxygen are sold annually in the United States, almost entirely for the oxyacetylene blow-torch.

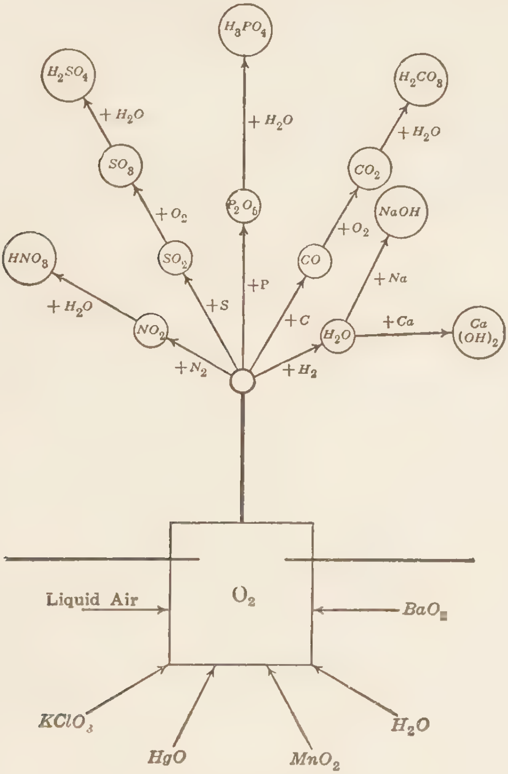
H_3PO_4
H_2SO_4
H_2CO_3
$+ H_2O$
$+ H_2O$
$+ H_2O$
SO_3
CO_2
$+ O_2$
P_2O_5
$+ O_2$
$NaOH$
HNO_3
SO_2
CO
$+P$
$+ Na$
$+ H_2O$
$+S$
$+C$
NO_2
H_2O
$+ Ca$
$Ca(OH)_2$
$+ N_2$
$+ H_2$
O_2
Liquid Air
BaO_2
$KClO_3$
H_2O
HgO
MnO_2

FIG. 12.—Oxygen tree.

Liquid oxygen mixed with fine carbon dust and oil is now being used as a mine explosive. Unexploded charges are not dangerous for, on standing, the oxygen evaporates.

A rather small quantity of oxygen is used in medicine to revive weakened patients and to administer with nitrous oxide ("laughing gas") when the latter is used as an anesthetic. Nitrous oxide alone would cause suffocation. Oxygen is also needed in submarines and caisson tunneling to replace that used up by the workman.

Industry is impatiently waiting for a cheap process of separating oxygen from the nitrogen of air. When that is achieved blast furnaces for making iron from ores will be operated with a blast of air enriched by added oxygen. For every ton of pig iron made five tons of air are required. The possibility of increased efficiency here is attractive.

Influencing the Speed of Reaction.—The speed of chemical reactions is greatly influenced by temperature, by the concentration of the reacting substances, by the presence of catalysts and by the amount of contact surface.

A rise in temperature of 10° doubles or trebles the speed of most reactions. A rise from 20° to 200° means a million-fold increase in velocity of reaction. This is understood when we remember that a rise in temperature means that the molecules move faster, consequently hit each other harder and oftener. Reactions probably continue at low temperatures but at rates too slow to observe. This temperature influence is familiar in cooking. In a pressure cooker with the steam retained by a tight lid tough meat is made tender at perhaps 125° in a fraction of the time required in an open vessel where the temperature would be little more than 100°.

The concentration of two substances thoroughly mixed also affects speed of reaction. It can be expressed quite simply in the phrase "opportunities for contact." If, for example, in a cubic centimeter there are one million molecules of A and one million of B, the reaction takes place at a definite speed. Now if the concentration of A be doubled, two million molecules in the cubic centimeter, it is obvious that the opportunities for contact between A and B will be doubled, that is, the speed of reaction will be doubled. If at the same time the concentration of B increase to three million molecules per cubic centimeter, the velocity of reaction must increase to 2×3 or 6 times. Charcoal and other combustibles burn more brilliantly in pure oxygen than in air because only one fifth of air is oxygen, and consequently pure oxygen at the same pressure has five times the *effective* concentration of air. Furthermore, much of the heat produced is absorbed in raising the temperature of the useless nitrogen.

With two substances that cannot be mixed thoroughly, such as a solid and a gas, the amount of surface of the solid is of great importance. Splinters or shavings burn much faster than a thick log—a matter of "opportunities for contact." Coal dust is now blown into cement kilns with air and burned like a spray of oil.

Each dust particle is in such good contact with air that combustion is rapid, and very high temperatures are attained. In fact coal dust "spray" is now burned in special boilers for steaming purposes. In the case of a solid and liquid mixture stirring speeds up reaction by bringing fresh molecules to the surface of the solid. One of the "heating powders" used as a convenient substitute for hot water in the common hot-water bottle is nothing but iron powder, which rusts rapidly in contact with air and water.

"Pyrophoric lead" is easily prepared by gently heating a test tube partly filled with dry lead tartrate while a gentle stream of illuminating gas (to keep out oxygen) is led down to the bottom of the horizontal test tube. After the contents of the tube (now reduced lead in finely divided form and with great surface) have cooled, a stopper is inserted to keep out oxygen until required. When this lead powder is sifted through the air it ignites spontaneously. Pyrophoric iron can be prepared in a similar manner.

Dust Explosions.—Danger from inflammable dusts occurs in industries handling flour, starch, grain, sulfur, coal, leather, alfalfa, sugar, soap, cocoa, fertilizer, feeds, in short, where any combustible material is ground into dry dust. In some years dust explosions have caused a loss of scores of lives and millions of dollars.

The dusts require definite ignition temperatures, and also have what might be termed the lower and upper limits of concentration. Ordinary corn starch dust can ignite with a mixture of approximately 0.007 ounces per cubic foot, or seven ounces per thousand cubic feet. The ignition temperature of pulverized sugar is 540° C.; flour 650° C.; and corn starch, 640° C. In certain dusts the rate of flame propagation has ranged from 2,000 to 6,000 feet per second, and pressures ranging from 270 pounds to 400 pounds per square inch have been measured.

A *catalyst* is a substance that aids or retards a reaction without itself being permanently changed. Some catalysts condense the reacting substances on their surface, thus bringing in the influence of increased concentration and possibly making the condensed molecules more active by weakening the attraction between the constituent atoms. In cigar lighters the vapors of methyl alcohol mixed with air pass over a thin platinum wire. There is little oxidation without the platinum, but with increased concentration on the platinum surface the heat of oxidation makes the wire incandescent, igniting the alcohol. Gas lighters are much the same. Other catalysts enter into reaction but are released in their original form by further reactions. Manganese dioxide aids the release of oxygen from potassium chlorate at 200° by reacting to form a compound that decomposes readily, releasing oxygen and the original manganese dioxide. Other solid catalysts compel a more effective arrangement or orientation of one of the reacting substances on its surface. It is evident that a very little of the catalysts can be used many times over, almost indefinitely, in fact. Platinum powder is an invaluable commercial catalyst, for by its aid sulfur dioxide is rapidly oxidized:

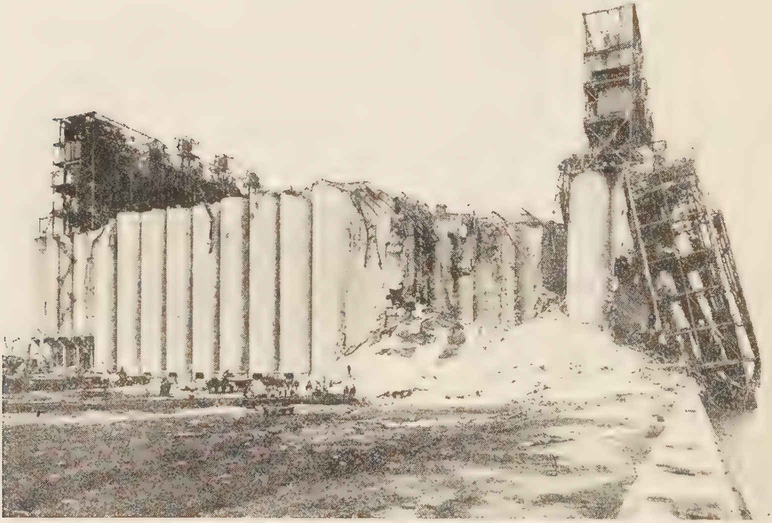

FIG. 13.—A grain elevator wrecked by a dust explosion.

$$2\,SO_2 + O_2 \longrightarrow 2\,SO_3.$$

The trioxide formed finally reacts with water to form sulfuric acid. Also nitrogen and hydrogen unite at a profitable rate with the help of special catalysts.

$$N_2 + 3\,H_2 \longrightarrow 2\,NH_3.$$

Since ammonia (NH_3) is valuable in making fertilizers and is easily oxidized by the further use of platinum as a catalyst to nitric acid, it is plain that catalysis is not a mere theoretical subject.

There are thousands of catalysts. Elements, oxides, acids, bases, and carbon compounds have been used to change the speed of reactions. In fact, we have recently discovered the action of "promoters," substances which increase the activity of the catalyst. Some of the famous explosive reactions fail to take place unless traces of water are present. Absolutely dry phosphorus will not burn in absolutely dry oxygen.

The Oxidation Process in the Animal Body.—" In muscular work," states A. V. Hill, "there is strong evidence that the immediate fuel oxidized is glycogen, $(C_6H_{12}O_6)_n$." During violent exercise large quantities of this glycogen are converted into lactic acid (the acid in sour milk), a sprinter running 100 yards at top speed producing about 30 grams. During the process of recovery this lactic acid is reconverted into glycogen. The muscle is capable of going into debt for oxygen. During a fast 100 yard dash the sprinter can breathe in only about twelve per cent of the total oxygen required for the effort. The chemical change from glycogen to lactic acid supplies the energy used, but the complete oxygen debt must be paid during rest or recovery. In a long race a man incurring an oxygen debt of 15 liters is incapable of further effort. Figure 14 shows the total oxygen requirement of a certain athlete during a 120 yard dash at various speeds. Great extravagance of energy is shown at high speeds. (First-class sprinters run about 30 feet per second.)

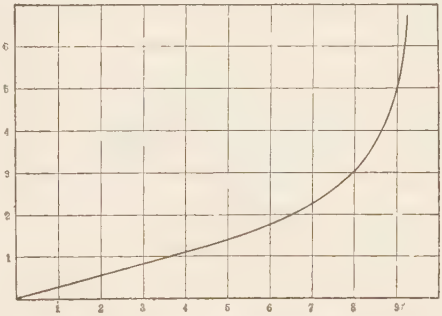

Fig. 14.—Oxygen demands (liters/min., vertical axis) by 139 lb. sprinter at speeds approaching 10 yds./sec. (horizontal axis).

Ozone

History.—Van Marum (1783) observed a peculiar odor near an electrostatic machine. Cruikshank (1801) noticed the same pungent odor in oxygen freshly made by the electrolysis of water, but failed to explain it. Schoenbein (1840) named the odor "ozone" (Greek "to smell"), but not until 1865 was its real nature discovered by Soret.

Occurrence.—There has been much argument as to the existence of traces of ozone in the air. Many writers repeat the original statement that the only times when perceptible quantities are found are during and immediately after a thunderstorm. Undoubtedly the lightning flash does generate a little ozone, but in the warm and moist air characteristic of thunderstorms ozone is quickly destroyed. It has been shown conclusively[1] that the atmosphere contains the most ozone not in summer but in winter. High barometric areas, which are merely whirling mountains of air, throw the upper air to the earth's surface faster than under any other conditions. As a result the ozone formed several miles up by the ultra-violet rays of the sun reaches the surface before it is all destroyed by heat, dust, and other agencies. Air is not very permeable to ultra-violet light and so the action of these rays from the sun is greatest in the upper layers. Cold, dry, and dustfree, the upper air gives a favorable environment for the existence of ozone. The stimulating effects of cold, "bracing" weather, when a "high" barometric area is passing over us, are due *in part* to ozone. We must be careful, however, not to overstate the benefits. Unscrupulous advertisers of health resorts often make extravagant claims.

Properties.—Ozone is a gas 1.5 times as heavy as oxygen, colorless, of a pungent odor, somewhat soluble in water and very soluble in turpentine, bluish when liquefied, and far more active chemically than oxygen. It even oxidizes silver if catalyzed by a trace of silver oxide. Ozone is rather explosive when highly compressed or liquefied. It is unstable at high temperatures, turning into oxygen. Three volumes of oxygen yield only two volumes of ozone which on decomposing (when heated above 280° C., for example) are changed back to the three volumes of oxygen. Since oxygen gas contains two atoms to the molecule ozone must contain three of the same atoms. The change from oxygen to ozone is expressed thus:—

$$3\,O_2 \rightleftarrows 2\,O_3.$$

When ozone oxidizes any substance it usually does so with the third atom, releasing a molecule of oxygen. Thus:

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[1] *American Chemical Journal*, Vol. 47, p. 497, 1912.

$$H_2S + O_3 \longrightarrow H_2O + S + O_2.$$

Preparation.—Although made in nature chiefly by the ultraviolet rays of the sun, ozone is produced in the laboratory and on a commercial scale by the silent electric discharge. When two plates of glass or other insulating material are placed parallel and close together with metal plates against the *outer* side of each, we have a simple ozone machine. An electric current will jump across the gap between plates *if* the potential or voltage is high enough. This high voltage is secured by the use of an induction coil. In the same way if a short section is removed from a water pipe the stream of water will jump the gap if the pressure of water is sufficiently great. Without the broad insulating plates the electricity would jump in the form of sparks, but with adequate insulating plates the discharge is "silent." In a darkened room a bluish glow is seen. If air or oxygen is passing between the plates some of the oxygen is transformed into ozone. A commercial ozonizer is made of a number of pairs of plates. For the laboratory two concentric tubes with tin foil on the inside of the smaller and on the outside of the larger may be made to serve very well (Fig. 15).

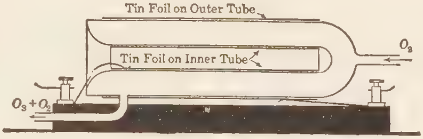

FIG. 15.—Ozone tube.

Since heat and the electric discharge decompose ozone into oxygen, it is the best economy to blow the ozonized air away with a fan.

At very high temperature oxygen changes into ozone, but so rapidly does the heat decompose the product that it is only by the most rapid cooling that any ozone can be detected. In this case heat energy if taken up while in the commercial ozonizer it is electric energy. It is no wonder, then, that ozone is more active than oxygen; it contains more energy. A gram of carbon burned in ozone thus releases more heat than a gram of carbon burned in oxygen. This additional heat comes from the decomposition of ozone.

$$3\,O_2 \leftrightarrows 2\,O_3.$$

A comparison of the heats of combustion of carbon in oxygen and ozone throws light on the preceding statements.

$$3\ C + 2\ O_3 \longrightarrow 3\ CO_2 + 352{,}000\ \text{cal.}$$
$$3\ C + 3\ O_2 \longrightarrow 3\ CO_2 + 283{,}200\ \text{cal.}$$

The difference in these heat values equals the heat of formation of two gram-moles of ozone, 68,800 calories.

The oxygen-ozone transformation equation shows that each substance changes into the other and yet explains how ozone can be both made and decomposed by high temperatures. Warburg states that at 16° C. 1 per cent ozonized oxygen decomposes in 1.7 minutes; at 100° in 0.003 minutes, and at 1000° almost instantaneously.

A simple laboratory method of preparing ozone is to drop concentrated sulfuric acid on barium peroxide. It is best to smell this cautiously because too much ozone is irritating. Possibly also a spray of minute drops of the acid may add to the irritation. Passing the gas through a loose wad of cotton or glass wool would catch any spray.

Fluorine reacts so violently with water that the oxygen released contains 14 per cent of ozone.

If a stick of moist white phosphorus is placed in a stoppered bottle of air (with some water in the bottle) ozone can be smelled, and can be detected in other ways. In fact it is said that the odor of unburned matches is the odor of ozone caused by the slow oxidation of phosphorus in the match.

Ozone is formed in all chemical reactions where atomic oxygen is released at low temperatures, in the absence of easily oxidized substances.

A platinum wire made incandescent in liquid air or oxygen converts, by thermal action, much oxygen to ozone because the product is promptly cooled and dissolved in the liquid oxygen.

The decomposition of potassium chlorate yields no ozone because the temperature is too high, but periodic acid heated to 130° produces oxygen rich in ozone.

Ozone doubles the "drying" speed of oil paints, varnishes, and certain inks.

Allotropic Forms of Elements.—A number of elements such as oxygen, hydrogen, nitrogen, phosphorus, sulfur, carbon, and iron are capable of existing in two or more forms, with different energy content and different physical properties but with unchanged chemical properties. These *allotropic modifications* (oxygen-ozone; white phosphorus—red phosphorus; etc.) of elements are made up of molecules containing different numbers of the same atoms or with different arrangements of atoms and different amounts of energy.

It has already been mentioned that electrolytic oxygen contains ozone. With dilute sulphuric acid of 1.1 density as electrolyte, as much as 17.23 per cent of ozone has been secured at very small, cooled anodes.

Uses.—Ozone has been used to sterilize water, to purify indoor air, to sterilize bandages, etc., in hospitals, to bleach oils, flour, delicate fabrics and in a few oxidation processes in chemical manufacture. It is easy to overstate these uses.

Tests.—Some authorities claim to smell one part of ozone in 10,000,000 parts of air, rivaling hunting dogs in keenness. A simple test is the development of blue color in a starch-potassium iodide paper:

$$O_3 + 2\ KI + H_2O \longrightarrow O_2 + I_2 + 2\ KOH.$$

Ozone releases free iodine, which then turns blue on contact with starch. Unfortunately any good oxidizing agent such as nitric acid or hydrogen peroxide will do this. But if the gas to be tested is slowly passed through a tube heated above 280° C., any ozone will be destroyed. This serves as a check on the test. Mentzel used "tetramethyl base" paper, which turned violet in ozone, yellow in nitrogen dioxide, and was not affected by hydrogen peroxide. Ozone darkens (oxidizes) a clean silver plate which has just been held in a flame to get a trace of oxide (catalyst).

EXERCISES

8. Compare the properties of oxygen and ozone.
9. Describe four methods of making oxygen.
10. What are oxides? Name some that are solids; liquids; gases.
11. Give two examples of an exothermic reaction.
12. What is catalysis? Examples?
13. Of what importance is it to fish that oxygen is slightly soluble in water?
14. How could you remove dissolved air from water?
15. How did Lavoisier prove that oxygen is one fifth of air by volume?
16. Burn 100 g. of magnesium (flash-light metal). Does the ash weigh more or less than 100 g.? How about a candle?
17. Why select oxygen as the first element to study?
18. What weight of oxygen may be obtained by heating 30 g. of barium peroxide?

√ 19. What percentage by weight of free oxygen is obtained by heating (1) mercuric oxide, (2) barium peroxide, (3) potassium chlorate? At \$1.50, \$1.00 and \$0.15 per Kg. respectively, which is the cheapest source of oxygen?

√ 20. How many grams of oxygen will be obtained by treating 95 g. of sodium peroxide with excess water?

√ 21. Calculate the percentage of oxygen in SO_2, SO_3, KNO_3, H_2SO_4 and $KClO_3$. Use the table of atomic weights.

√ 22. Compare the weights of oxygen required to combine with 15 g. each of phosphorus and sulfur.

23. Complete these statements: Phosphorus pentoxide is the .... of phosphoric acid. Calcium oxide is the .... of the base, calcium hydroxide.

24. Why do you suppose Lavoisier stopped heating the mercury at the end of twelve days and why didn't he quit at the end of a week?

25. Define a metal; a non-metal.

26. Define combustion; spontaneous combustion.

27. How does paint "dry"?

28. How does the blood function in oxidation of animal tissues?

29. Why does coal dust burn quietly in air but explode when mixed with liquid oxygen and detonated with a cap?

30. How can a reaction be speeded up?

31. What makes ozone in the upper air?

32. What are the properties and uses of ozone?

33. If 68,390 cal. of heat are released when 2.016 g. of hydrogen unite with 16 g. of oxygen to form 18.016 g. water, how much heat (or its equivalent in electricity) would be required to decompose 18.016 g. of water?

34. What precautions should be taken to prevent dust explosions in factories and coal mines?

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NOTE: Ozone also differs from hydrogen peroxide and the oxides of nitrogen in its ability to bring back the fluorescence to a basic solution of reduced fluorescein. This excellent qualitative and quantitative test is described in the *Journal of Chemical Education*, *6*, 1350, (1929), and in the *Analyst*, *54*, 189, (1929).

REVIEW SUGGESTIONS

You have now studied four chapters. It is time to form the invaluable habit of *constantly reviewing.* Out of every two hours you use in preparation for a lecture spend one-fourth of the time, half an hour, in review and make it the *first half-hour.* Otherwise you will find the time gone on the advanced lesson with no review. Your intention to catch up some day will be excellent, but such intentions are too often not made good.

Write equations constantly. Repeat those in the text and think up others to describe every reaction you have observed.

Do not read your lesson three times and assume that because you clearly understood every statement as you read it you have a thorough grasp of the chapter. The test of your knowing the lesson is this: Can you shut the book and write an outline of the leading topics and then tell to yourself the leading facts under each topic head? Be as critical of your knowledge as your teacher may be on quiz day. Most students pamper themselves.

Skim the chapter to get a bird's-eye picture of it. Then carefully read the first topic once, shut the book, and tell yourself the main points of that topic. See if you are right. Read the next topic the same way. On finishing the last topic you will know the lesson.

Do not commit to memory the atomic weights. You will learn formulas by using them. Remember only the most important properties of substances.

Get a friend to open the text and quiz you on some chapter. Then quiz him on another chapter. Pretend to be stupid so that he will be forced to painful clearness in his answers. He can try this strategy on you.

CHAPTER V

GASES, LIQUIDS, AND SOLIDS

Gases

The compression of liquid water to four-fifths of its original volume requires 10,000 atmospheres. It is a significant fact that any gas spreads (diffuses) through any other gas with great ease, almost as if the second gas were not occupying the given space. When we add the characteristic of non-settling to such properties of gases as a great tendency to expand, great compressibility, great diffusibility and great permeability, we are forced to explain how the structure of gases differs from the structure of liquids and solids. The gas laws immediately following lead into the kinetic theory of gases.

Boyle's Law.—Boyle (1660) observed that ***the volume occupied by the same sample of any gas varies inversely with the pressure.*** Accurate measurements showed him that if he doubled the pressure on a liter of a gas (keeping the temperature constant) the volume became only half a liter. With three times the pressure the volume became one third of a liter. This generalization can be formulated mathematically thus:

$$\frac{P_1}{P_2} = \frac{V_2}{V_1} \quad \text{or} \quad P_1V_1 = P_2V_2 \quad \text{or} \quad V_1 = V_2 \times \frac{P_2}{P_1},$$

where P_1 and V_1 are the first pressure and volume and P_2 and V_2 any other pressure with its accompanying volume. Since the product P_1V_1 is equal to any other pressure-volume product for the same weight of the gas, it is sometimes said that the product of the pressure times the volume of a gas is a constant. It is our custom to refer to the average atmospheric pressure at sea level (enough to hold up a 760 mm. column of mercury in a barometer) as the standard pressure.

The simplest form of a barometer (on the right in Fig. 16) consists of a tube, over 760 mm. long, filled with mercury and inverted in a cup of mercury. The pressure of the air holds up the mercury in the tube to a height of about 760 mm. at sea level. If the tube is longer, there is a vacuum at the top. The cup may be dispensed with by using the form of tube represented on the left.

Atmospheric pressure varies with the weather, the passage of high and low barometric areas sometimes causing a variation of 50 mm. or more in the barometric reading.

A man buying a million liters of a rare and expensive gas could be cheated if he failed to stipulate the pressure. Since gases expand indefinitely, even a very small weight of a gas could occupy a million liters volume. We do not always measure gases at exactly 760 mm. pressure, but we calculate from Boyle's law what the volume would be if the pressure were changed to the standard 760 mm. For example, 400 cc. of air at 740 mm. would occupy what volume at 760 mm.? Using the formula

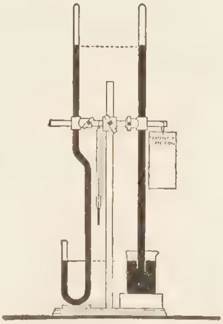


FIG. 16.—Two forms of mercury barometer.

$$V_1 = V_2 \times \frac{P_2}{P_1},$$

we may let V_1 represent the volume to be calculated and P_1 the standard pressure, 760 mm. To make it clearer

$$V_1 \text{ (standard)} = V_2 \text{ (observed)} \times \frac{P_2 \text{ (observed)}}{P_1 \text{ (standard)}}.$$

Substituting, we have

$$V_1 \text{ (standard)} = 400 \times \frac{740}{760} = 389 \text{ cc.}$$

To aid the memory one merely recalls that the observed volume is multiplied by a fraction with the two pressures for its terms. Also if the change to 760 mm. means *greater* pressure, the gas will contract and therefore the numerator must be the smaller value. The calculation is similar if the change to 760 mm. means *less* pressure and consequent expansion.

EXERCISE 1.—Convert 420 cc. of dry gas at 740 mm. to the volume at 760 mm.

EXERCISE 2.—Convert 800 cc. of dry gas at 768 mm. to the volume at 760 mm.

High Vacua.—In spite of the great efficiency of devices for removing gas molecules from vessels, scientists have never yet obtained a vacuum in which one cubic centimeter included fewer molecules than there are people on the earth.

The Langmuir vacuum pump operating on the mercury vapor condensation principle, is used in connection with a backing pump capable of exhausting gases to a pressure only sufficient to hold up a column of mercury 0.1 mm. in height. With this as a start a further vacuum of 0.000002 mm. is readily obtained. "If from a liter vessel of gas there were removed 1,000,000 molecules a second, nearly 700,000,000 years would be required for the removal of practically all of the gas; but the Langmuir pump accomplishes this in two seconds." High vacua, or even partial vacua, minister to our comfort and serve well in many ways. They made possible the original incandescent lamp (although the type has since changed), the X-ray tube, the radio tube, the photoelectric cell of television, the thermos bottle, suction pumps, and increased the efficiency of steam engines and turbines.

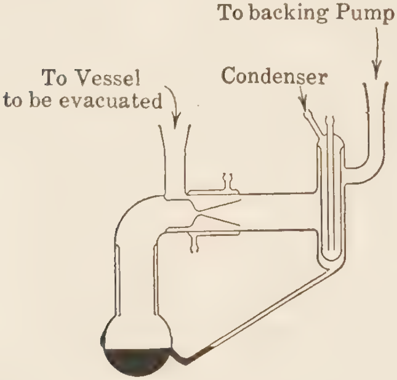


Fig. 17.—A vacuum pump that uses a stream of vapor from boiling mercury (condensed and returned) to sweep out gases.

Charles' Law and the Absolute Temperature.—Charles in 1787 observed that on cooling any gas from 0° C. to −1° C. it contracted 1/273 of its volume. It was a simple inference that if cooled 273° C. its volume would be nothing at all. However, in practice all gases become liquid before they have been cooled 273° C. below 0° C., and after it becomes liquid a substance no longer obeys the gas laws. The most difficult gas to liquefy was helium, which had to be cooled to −268.7° C. There is a real convenience however, in calling this imaginary point of no volume *absolute zero* −273° C.

Onnes induced an electric current in a lead ring at 1.7° Abs., The electric resistance was so low that current continued to flow for some time after the exciting cause was gone.

Although Onnes cooled helium, by evaporation of its own liquid form, to within one degree of absolute zero, he believed that it would remain fluid even at 0° Abs. However, in July 1926, only a few months after the death of Onnes, his associate, Keesom at the University of Leiden, froze helium to a solid at 0.9° Abs. under 128 atmospheres pressure.

Figure 18 shows the relations between the two temperature scales. To change from a Centigrade reading we merely add 273°

to get the absolute temperature. For example, 17° C. = 17° + 273° = 290° Absolute.

Exercise 3.—Convert −25° C. into the absolute temperature.

Charles' law is merely an observation that ***the volume of a given sample of a gas varies directly as the absolute temperature*** (if the pressure is kept constant). For example, to double the volume that a gas occupies at 20° C. by heating we should need to heat not to 40° C. but to double the absolute temperature. The temperature 20° + 273° = 293° Absolute; so double this temperature would be 586° Absolute or 313° C.

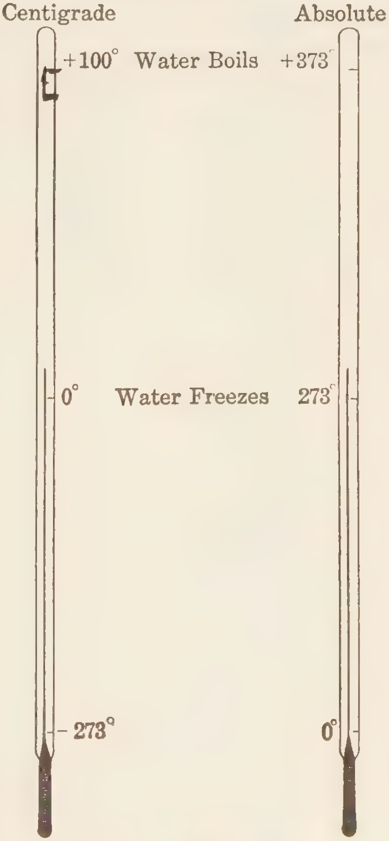


Fig. 18.—Centigrade and absolute thermometers.

When heated to 313° C. the gas would have twice its original volume. Charles' law is, therefore, formulated as follows:

$$\frac{V_1}{V_2} = \frac{T_1}{T_2} \quad \text{or} \quad V_1 = V_2 \times \frac{T_1}{T_2},$$

where T_1 and T_2 refer to absolute temperatures. When we speak of a liter of oxygen weighing 1.429 g. we mean a liter at 760 mm. pressure and 0° C. Since gases expand on heating, there can be no accuracy without reference to a definite *standard temperature.* Obviously we do not care to measure gases in rooms at 0° C., but we can apply Charles' law and calculate what the volume would be if the gas were cooled to 0° C. For example, what is the volume of 400 cc. of air measured at −18° C. when warmed to 0° C.?

$$V\ (\text{standard}) = V\ (\text{observed}) \times \frac{273}{273 \pm t^\circ}$$

where $t°$ is the Centigrade temperature. Substituting values,

$$V\text{ (standard)} = 400 \times \frac{273}{255} = 428\text{ cc.}$$

When confused one can recall that the observed volume is multiplied by a fraction with absolute temperatures for its terms and that if the change is to a *higher* temperature the gas will expand, occupying more volume; therefore the numerator must be larger than the denominator. The observed volume of a gas can be brought to 760 mm. and 0° C. by applying both connections at once. For example, 400 cc. of air at 740 mm. and $-18°$ C. would have what volume standard?

$$V\text{ (standard)} = V\text{ (observed)} \times \frac{740}{760} \times \frac{273}{255} = 417\text{cc.}$$

It also follows from Charles' law that for each degree rise in temperature the pressure of a gas increases by 1/273 if the volume is kept constant.

When gasoline explodes (with air) in an auto engine approximately 58 volumes of all the gases concerned are converted into new substances that would occupy about 62 volumes if kept at the same temperature as before. The enormous increase in pressure actually observed must be due to the high temperature of reaction which makes the molecules (almost the same number as before) move with greater velocity.

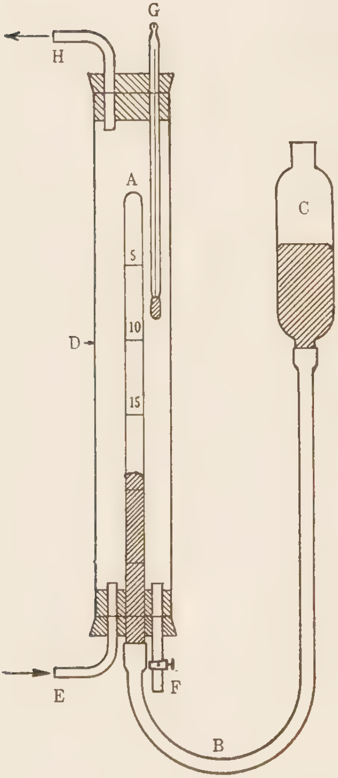


Fig. 19.—Mortimer's apparatus for demonstrating Charles' Law and Boyle's Law. The pressure on air confined in A is changed by moving the mercury reservoir C. The temperature is changed by a stream of vapors or liquids in D. (*Journal of Chemical Education, 4, 781, (1927)*).

Exercise 4.—Convert 180 cc. of dry gas at 14° and 775 mm. to its volume at 0° and 760 mm.

The pressure required to prevent expansion of a gas on heating varies directly as the absolute temperature.

Temperature Measurements.—Boiling point of oxygen, −182.97° C.; boiling point of sulphur, 444.60° C.; melting point of silver, 960.5° C.; melting point of gold, 1063° C.; are the fixed temperatures which, in addition to the melting and boiling points of water, 0° C. and 100° C. respectively, have been adopted by the U. S. Bureau of Standards, and other national laboratories, for a standardized temperature scale.

Using an electrical heat-measuring device so incredibly delicate that it is sensitive to two trillionths of an ampere of current and will measure temperature changes of as little as one ten-millionth of a degree Centigrade, A. V. Hill of the University of London has measured the temperature changes in nerve fibers during their activity.

Law of Partial Pressures.—Dalton noted that the total pressure of a mixture of gases was the sum of the pressures that would be exerted by each gas if the others were not present (temperature being the same). All gases collected or measured over water have water vapor present, which exerts a part of the total pressure. To learn the actual pressure exerted by the dry gas we must subtract the pressure due to water vapor at the given temperature. To show how the values for the pressure of water vapor can be obtained we can fill a tube over 760 mm. long with mercury and, closing the end with

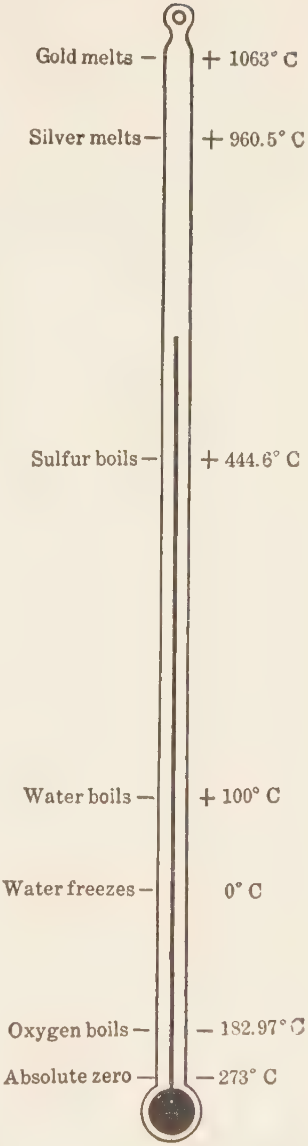


FIG. 20.—A standard scale of accurately determined temperatures. Of course a mercury thermometer would not serve above 350°.

a thumb, invert the tube, placing the open end in a dish of mercury. The mercury is held up to some definite height, depending on the pressure of the air, 760 mm. at sea level. We have thus a simple form of the *barometer* for measuring air pressures. If, now, we force a few drops of water (by a medicine dropper) under the tube, the water rises into the vacuum at the top, turns to vapor, and exerts pressure downward on the column of mercury. The mercury falls several millimeters, depending only on the temperature. To determine the pressures at different temperatures the tube can be surrounded with a jacket through which flows water at desired temperatures. A table of "aqueous tension" values is given in the Appendix. Since we measure most gases over water, the gases are saturated with moisture at the given temperatures. Suppose the problem is to correct to standard conditions 400 cc. of air collected over water at 740 mm. and 18° C. Now the *observed pressure* of 740 mm. is not all due to the air, for 15.5 mm. of it is due to water vapor. Therefore

$$V_1 \text{ (standard)} = V_2 \text{ (observed)} \times \frac{740 - 15.5}{760} \times \frac{273}{291} = (?) \text{ cc.}$$

NOTE: A table of corrections for the expansion of the mercury column due to heating above 0° C. is found attached to the barometer.

EXERCISE 5.—Convert 200 cc. of air measured over water at 23° and 780 mm. to the volume under standard conditions.

A general equation for all such problems is given below:

$$V_1 \text{ (stand.)} = V_2 \text{ (obs.)} \times \frac{P_2 \text{ (obs.} - \text{aq. tension)}}{P_1 \text{ (stand.} = 760 \text{ mm.)}} \times \frac{T_1 \text{ (stand.} = 273° \text{ C.)}}{T_2 \text{ (abs.} = 273° \text{ C.} \pm t° \text{ C.)}}.$$

Graham's Law of Diffusion.—All gases mix homogeneously unless they react. Bromine is a heavy gas, but if a little is released at the bottom of a tall cylinder of air the bromine can soon be smelled at the top, rising against the force of gravitation. Finally the air and bromine will be uniformly mixed. Hydrogen is the lightest gas, and yet if some of it is released at the top of a tall closed cylinder of air the hydrogen will diffuse to the bottom and a uniform mixture result. It is an interesting but unfortunate fact that the helium gas in a dirigible balloon diffuses out slowly while air diffuses in.

Graham measured the rates at which gases diffuse through minute holes and found that *the speed of diffusion of gases varies inversely as the square roots of their densities.* Oxygen is about sixteen times as heavy as hydrogen, hence hydrogen diffuses four times as fast as oxygen. Let R_1 represent the rate of diffusion for oxygen and R_2 the rate for hydrogen; D_1 the density of oxygen and D_2 the density of hydrogen:

$$\frac{R_1}{R_2} = \frac{\sqrt{D_2}}{\sqrt{D_1}} = \frac{\sqrt{1}}{\sqrt{16}} = \frac{1}{4}.$$

Exercise 6.—A liter of carbon dioxide weighs 1.9768 g. and a liter of nitrogen weighs 1.2507 g. Compare their rates of diffusion accurately

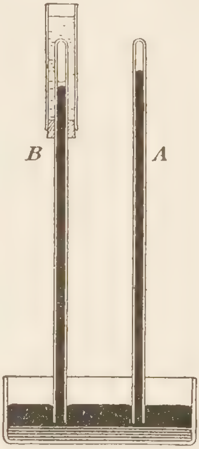


Fig. 21.—Use of a jacketed barometer in determining vapor tension of water at different temperatures.

The Kinetic Theory of Gases.—To explain the facts expressed in the laws of Boyle, Charles, and Dalton, as well as certain other facts, it is believed that the molecules of a gas are relatively very far apart, moving rapidly in straight lines until they collide with other molecules, yet rebounding with such perfect elasticity that there is no loss of motion. At 20° C. a single H_2 molecule collides with its fellows 10 million times per second. Cohesion in a liquid retards molecular motion but in a gas it has very little effect since gaseous molecules are relatively far apart. Pressure is due to the impacts of molecules. The velocity of molecular motion is increased by rise in temperature.

Since all gases react alike to change in pressure and temperature, they must all have the same structure. The enormous compressibility of gases is strong evidence in favor of the kinetic theory. On this assumption compression merely means a decrease in the spaces between molecules—bringing molecules closer together. Reliable experimental evidence has recently shown that at 0° C. and 760 mm. 1 cc. of any gas contains 2.7×10^{19} molecules and yet the average distance between molecules is about thirteen times their average diameter.

Imagine a one-liter cylinder closed with a smoothly moving plunger. If the pressure exerted by the plunger is doubled by adding weights, the plunger sinks to the halfway mark and the volume of the gas becomes one-half a liter. Now the plunger is upheld by the opposing pressure of the gas which has just been doubled. Why? Obviously the same number of molecules is contained in one-half the space after the extra compression. This means that twice as many molecules strike the plunger per second as before, thus ***accounting for the fact of doubled pressure.***

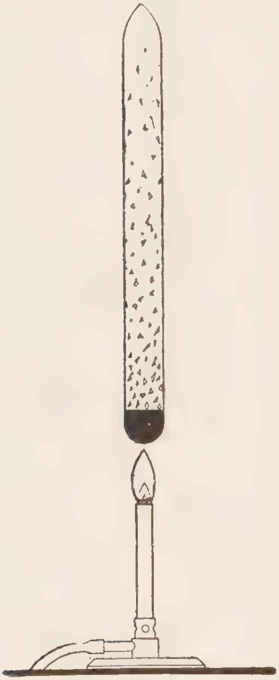


Fig. 22.—In this glass tube mercury and some small bits of blue glass were sealed in a moderate vacuum. When the mercury is cautiously heated, without boiling, the increased molecular bombardment by mercury molecules knocks the bits of glass to the full height of the tube, possibly 25 cm.

As was stated before a very small mass of any gas expands indefinitely, filling any vessel no matter how large. Pressure is exerted on the cover of such a vessel. This could not be true if gases exerted pressure like the thrust of a spring or the downward and sidewise thrust of a liquid. Gas pressure is exerted in all directions and has no limit in distance. The spring has its limit. The theory that gas pressure is produced by the impacts of separate moving particles is in accord with the facts of gas pressure. The walls of containing vessels are pounded with a hailstorm of particles moving at 0° C. at a speed of one quarter of a mile per second.

At ordinary temperature the hydrogen molecule moves about one mile per second, but in that distance it suffers millions of collisions with its neighbors. Were it not for the perfect elasticity of molecules this great velocity would rapidly drop to nothing.

Heat is merely the evidence of molecular motion. ***Absolute zero*** now takes on a new meaning. It is the temperature of no molecular motion. A rise in temperature increases pressure by increasing the kinetic energy of the flying molecules, which equals $\frac{1}{2}\ ms^2$ (where m is the mass and s the speed of the molecule). But such experiments as weighing a closed vessel full of gas at different temperatures show no change in m, therefore it is only the speed that changes with temperature.

The open structure of gases explains their ease of diffusion and perfect mixing. It also explains the Law of Partial Pressures. No wonder each gas in a mixture can bombard the walls of containing vessels just as readily as if other gases were not present. There is enough of free space between molecules to permit other particles to move freely.

Cohesion between molecules of a gas counts for very little because they are so far apart and, at elevated temperatures, moving with such great velocity. But on cooling, their kinetic energy decreases and the molecules come close enough to each other to allow their mutual attraction (cohesion) to become a powerful factor. The gas may then become a liquid. At very high pressures, then, gases decrease in volume more than could be predicted by Boyle's law, due to this helping effect of cohesion. There is another factor which introduces a deviation from the gas laws. At ordinary pressures a liter of gas is mainly space, but when highly compressed the part of the total volume occupied by actual molecules becomes noticeable. Since Boyle's law holds only for the change in free space, it loses in accuracy at high pressures. The extent of deviation is shown for several gases in the following table.

The volumes indicated are those occupied at 0° by two liters of each gas when the pressure is increased from one atmosphere to two atmospheres. They should all be exactly one liter if Boyle's law held perfectly.

Hydrogen	1.0006 liters
Nitrogen	0.9996 liter
Oxygen	0.9991 liter
Carbon dioxide	0.9931 liter
Ammonia	0.9845 liter
Sulfur dioxide	0.9739 liter

The gases that are liquefied most easily, such as ammonia and sulfur dioxide, depart farthest from this law. At high pressures a point is reached where all gases that do not liquefy are compressed less than they should be in accordance with this law. The greater compressibility under moderate pressures is caused by the attraction of molecules for each other—the same forces which cause the gas to liquefy at low temperatures or under pressure.

The point of too little compressibility is reached when the molecules are brought so close together that the molecules themselves fill a considerable fraction of the total space.

In liquids and solids cohesion is a tremendous factor because the molecules are in frequent contact. Yet the molecules are moving even here, although in shorter free paths. Evaporation of liquids, their vapor pressure, and the fact that increase of temperature transforms solids and liquids into gases, all confirm this view. Mercury is easily volatilized, but we are thankful that tungsten is not, for otherwise tungsten electric lamps would not last long. Sugar, as we have learned already, decomposes without volatilizing.

Van der Waal's Equation is a correction of Boyle's law based upon allowance for the forces of cohesion and the actual space occupied by the molecules.

$$PV = P_1V_1 \text{ (Boyle's law).}$$

Since this merely states that at any fixed temperature the product of the pressure times the volume of a gas has a constant value (no matter if either the pressure or volume changes) we can conveniently represent this actual constant value by the symbol K. Then Boyle's law may be written

$$PV = K.$$

Actually the space through which each molecule is free to move must be less than V, that is $V - b$ where b represents the actual volume of the molecules themselves.

V = total volume
b = volume occupied by molecules
$V - b$ = free volume between molecules

Now the attraction of molecules for each other becomes an increasingly important factor, as the density increases, thus aiding compression. Of course this cohesion varies directly as the square of the density or inversely as the square of the volume occupied by a definite weight of a gas. The total pressure, then, is the sum of the observed pressure and this intermolecular attraction.

a = intermolecular attraction at a given volume
$\frac{a}{V^2}$ = intermolecular attraction for any other volume

$$P + \frac{a}{V_2} = \text{total pressure}$$

$$\left(P + \frac{a}{V^2}\right)(V - b) = K \text{ (Van der Waal's Equation)}$$

Critical Temperature.—On compression gaseous molecules can be brought so close together that their own attractive forces restrict their motion greatly and liquefaction results. The lower the temperature the less the pressure required to overcome the kinetic energy of the molecules. Yet for every gas there is a temperature above which no pressure, however great, can overcome this kinetic energy and produce liquefaction. This is called the *critical temperature.* The pressure required to liquefy a gas at its critical temperature is its *"critical pressure."*

GAS	CRIT. TEMP.	CRIT. PRESSURE
Hydrogen	51.0° Abs.	13.4 atmospheres
Nitrogen	128.0° "	33.5 "
Oxygen	155.0° "	49.5 "
Carbon dioxide	304.0° "	72.9 "
Ammonia	405.9° "	112.3 "
Chlorine	419.0° "	83.9 "
Sulfur dioxide	430.0° "	77.7 "

Avogadro's Law.—All the preceding facts, and some others to be considered later, led Avogadro in 1811 to the theory that *equal volumes of all gases at the same temperature and pressure contain equal numbers of molecules.* Until 1860 science paid little attention to this speculation, but we are now convinced of its truth.

The Three States of Matter.—Solids retain their shape, liquids take the shape of the containing vessel, while gases expand indefinitely. There is great freedom of molecular movement in gases and comparatively little in solids and liquids. Whether a substance is in the solid, liquid, or gaseous state at a given temperature and pressure depends on the relative influence of the forces of cohesion and the kinetic energy of the molecules.

Transformations.—Kinetic energy must be consumed in order to bring about the change:

$$\text{Solid} \longrightarrow \text{liquid} \longrightarrow \text{gas.}$$

The forces of cohesion must be overcome in order to allow the increased freedom of molecular motion called for by the change of state.

LIQUIDS

In liquids there is no orderly arrangement of molecules (with the exception of the rather unusual liquid crystals). Yet in such liquids as water, alcohol and acetic acid some of the molecules are "*associated*" in groups, the proportion of such associated molecules varying with the temperature. Steam, for example, is made up of single molecules, while liquid water contains $(H_2O)_3$ as well as $(H_2O)_2$ and simple H_2O. The freedom of movement by molecules in liquids is such that at the surface molecules with sufficient kinetic energy fly off into the space above, or, in other words, *evaporate*. Some of these fugitive molecules, now in the vapor state, return to the liquid (because of the irregular molecular paths) and are held, at least temporarily, by the forces of cohesion. The rate of evaporation increases with rise in temperature, showing a steady increase in vapor pressure of the liquid until the upward thrust of escaping molecules equals the downward thrust of all gaseous molecules immediately above the liquid surface. At this temperature the liquid boils.

Boiling Point.—The boiling point of a liquid is the temperature at which its vapor pressure just equals the pressure of the atmosphere above it. Obviously it varies with the pressure of the atmosphere. Water boils at 100° under an atmospheric pressure of 760 mm., but at one-half an atmosphere it boils at 82° while at two atmospheres the boiling point is 121°. Boiling points recorded in the text all refer to the standard atmospheric pressure, 760 mm. The ebullition observed in any boiling liquid is due to the expansion of bubbles of vapor forming within the liquid.

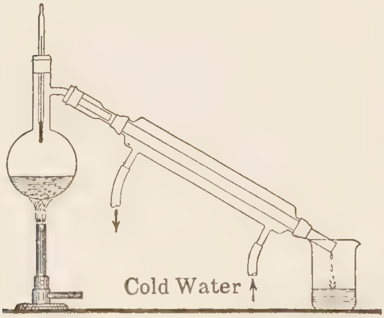


Fig. 23.—Purifying water by distillation.

Boil the water in a strong, round-bottomed flask partly filled with the liquid. Shut off the gas and quickly stopper the flask. Of course the ebullition stops at once, not only because of the fall in temperature, but also because retention of the steam increases the pressure on the surface of the water, raising the boiling point above 100° C. Invert the hot flask under a stream of cold water. The water boils again because the condensation of the vapor above the liquid decreases the pressure.

Distillation.—The process of evaporating and recondensing a liquid (by cooling) is termed *distillation*. To expedite matters the liquid is usually boiled, sometimes under less than atmospheric pressure. This *vacuum distillation* is desirable with liquids or solutions likely to decompose at the normal boiling temperature. Of course with diminished pressure of vapors above a liquid less kinetic energy and a lower temperature is required for boiling. In Figure 23 is shown ordinary laboratory distillation.

Fractional Distillation.—Separation of a mixture of liquids by fractional distillation is based on the difference in volatilities of the various constituents. For example, at atmospheric pressure pure ethyl alcohol boils at 78.4 deg. C. while pure water boils at 100 deg. C. The two are miscible in all proportions, and the boiling point of a mixture of ethyl alcohol and water will be between 78.4 and 100 deg. C., the boiling points of the pure constituents. The higher the proportions of ethyl alcohol the nearer will the boiling point of the mixture approximate 78.4 deg. C., the boiling point of absolute (chemically pure) alcohol.

Experiments show, for example, that a mixture of 50 per cent pure ethyl alcohol and 50 per cent pure water, by volume, boils at 82.81 deg. C. The vapors formed during this evaporation, however, will not consist of 50 per cent of alcohol and 50 per cent of water, but they will contain 74.95 per cent of alcohol and only 25.05 per cent of water. The vapors will be richer in the more volatile constituent, ethyl alcohol in this case. As a general rule, vapors formed from a mixture of miscible liquids are richer in the more volatile constituent than the original liquid.

The following figures show the composition of the vapors, in per cent, by volume, of ethyl alcohol from various strengths of liquids. (Sorel's table):

C_2H_5OH in Liquid Per Cent	C_2H_5OH in Vapors Per Cent
5	35.75
10	51.00
20	66.20
30	69.26
40	71.95
50	74.95
60	78.17
70	81.85
80	86.49
90	91.80
100	100.00

It is evident that when a mixture of these liquids is gradually diminished in volume through vaporization, the liquid residue becomes poorer and poorer in alcohol, because larger proportions of alcohol leave with the vapors than were present in the liquid originally.

The reverse process is just as true. If vapors containing 69.26 per cent of alcohol condense, the first drop of liquid will contain 30 per cent of alcohol. Consequently the residual vapors become richer and richer in alcohol, because the proportions of alcohol in the condensate are smaller than in the original vapors.

Finally, we must state a very important law of chemistry—namely, that vapors in intimate contact with a liquid have always a composition which is directly related to the composition of the liquid. Referring to the above table, we may note that vapors containing 69.26 per cent of alcohol cannot be in intimate contact with a liquid which contains more or less than 30 per cent of alcohol. If the liquid contains more, for example, it will give up some of this alcohol to the vapor, and some of the water in the vapors will condense until equilibrium is established between the liquid and the vapor phases.

Fig. 24 shows graphically the above table. It shows the percentage of liquid which may co-exist with a definite strength of alcoholic vapors.

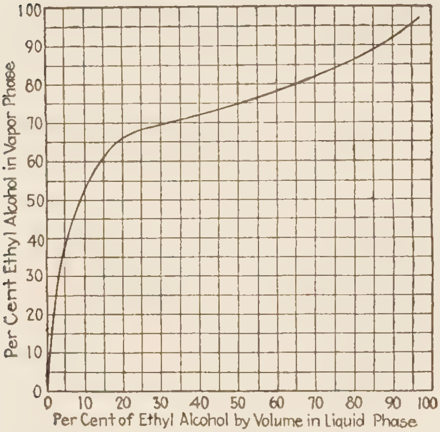


Fig. 24.—The distillation curve for alcohol-water mixtures. (From E. J. Winter, *Chem. Met. Eng.*, *30*, 18, 1924.)

Surface Tension.—The surface film of a liquid is in a state of tension due to the unbalanced attractions between molecules at the surface as compared with those which are entirely surrounded by other molecules. The molecules in the surface layer of liquid are attracted downward and sideways, not upward, since there are no liquid molecules above them (Figure 25). Consequently, the surface molecules act as if they formed a tightly stretched but elastic skin over the surface of the liquid.

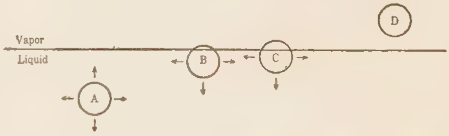


Fig. 25.—The molecular forces at and near the surface of a liquid.

As a result of this *surface tension,* a force acting parallel to the surface, every liquid tends to assume the spherical shape, because the sphere, of all shapes, has the least surface. Allow mercury, ether or other liquids to flow from a tube with a tip 0.1 mm. in diameter. Mercury runs in drops but ether in a stream.

Viscosity.—The term *viscosity* is used to denote the resistance due to internal friction which viscous substances offer to deforming forces. (A viscous substance is deformed permanently to a degree directly proportional to the deforming force.) Molasses and glycerin are typically viscous liquids, although their viscosity decreases with rise in temperature—they become more "fluid."

A viscous liquid will start to flow, no matter how small a pressure is applied, while with plastic solids no flow takes place until after the pressure has exceeded a certain definite "yield value."

The *liquefaction of gases* is discussed in detail on page 57 while *refrigeration* by rapid evaporation of very volatile liquids is introduced in the ammonia chapter.

SOLIDS

Freezing Point of Liquids.—On cooling liquids sufficiently they all lose their fluidity and take on rigidity. They freeze to solids without further lowering of temperature until all the liquid has solidified. When the change of state occurs at a definite temperature the solid formed is always crystalline.

Glasses and tars, however, do not change suddenly at a sharply definite temperature. In fact they act like undercooled liquids. Glycerine, suddenly chilled in liquid air, solidifies before it has time to crystallize, becomes glass-like. Even water may be chilled below 0° sometimes without separation of ice crystals. However, the addition of a minute fragment of ice starts crystallization or freezing. Consequently we are forced to define the freezing point (same as melting point) as the temperature at which liquid and solid will remain in contact with each other without change of temperature.

Melting Point and Heat of Fusion.—To increase the freedom of movement of the molecules of a solid so that a fluid results, requires increased kinetic energy. This is given by heating the solid. Heat breaks up the crystalline arrangement of a solid. There is a rise in temperature until some liquid is formed and then no further rise until all the solid is melted. Any additional kinetic energy given the liquid is used in tearing off molecules of the solid. To convert one gram of ice at 0° into liquid water, 79 cal. of heat are required. This is termed the *heat of fusion* of ice. The corresponding value for sulfur is 9.37 cal. and for aluminum 76.8 cal.

If a solid contracts on melting, any increase of pressure must lower the melting point. Thus ice at 0° is converted into water by considerable increase in pressure. On release of this pressure the water changes back to the solid form.

Vapor Pressure of Solids.—At the surface of solids there is less freedom of movement than at liquid surfaces and yet molecules evaporate from many solids. Wet clothes dry at temperature below 0° C., a crystal of iodine left in the open disappears, evaporates, and shows a very noticeable vapor pressure. An attempt to melt camphor or iodine at ordinary pressures fails to yield the liquid condition, merely increases the rate of evaporation. Solids that pass directly into the vapor state without melting are said to be ***sublime.***

Crystal Systems.—When a liquid solidifies it is usually found to be made up of particles of regular geometric form called crystals. Crystals are also formed by evaporation of solutions and cooling of some vapors. Crystals often mass together so as to make their individual forms indistinct, that is, we have a crystalline mass. Perfect crystals have plane surfaces meeting at definite angles and their edges are straight lines. There are so many different shapes known that the subject of crystallography may seem hopeless. However, these plane surfaces are arranged with reference to imaginary lines, called axes of symmetry, drawn through the crystal. There are only six arrangements of these axes, so there are only six crystal systems.

1. Isometric or cubic system: three axes of equal length at right angles to each other (Fig. 26). Examples: alum, sodium chloride, and potassium iodide.

2. Tetragonal system: two equal axes and one of different length, all at right angles to each other (Fig. 27). Example: nickel sulfate.

3. Rhombic system: three unequal axes, all at right angles (Fig. 28). Examples: sulfur, zinc sulfate, magnesium sulfate, and potassium nitrate.

4. Monoclinic system: two axes at right angles and a third at right angles to one but inclined with reference to the other. The axes may vary in relative lengths (Fig. 29). Examples: gypsum, sodium carbonate, oxalic acid, and potassium chlorate.

5. Triclinic system: three axes all inclined toward each other and of any relative lengths or inclinations (Fig. 30). Examples: calcium thiosulfate.

6. Hexagonal system: three equal axes in the same plane intersecting at angles of 60° and a fourth at right angles to all of these (Fig. 31). Examples: quartz, sodium nitrate, beryl.

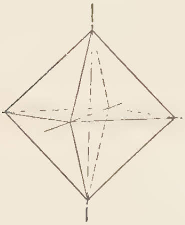


Fig. 26.—Cubic.

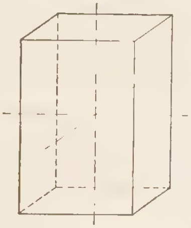


Fig. 27.—Tetragonal.

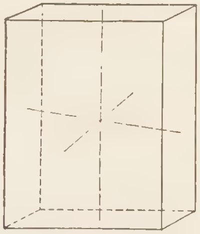


Fig. 28.—Rhombic.

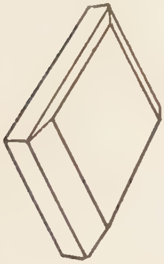


Fig. 29.—Monoclinic.

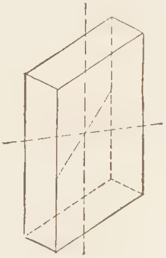


Fig. 30.—Triclinic

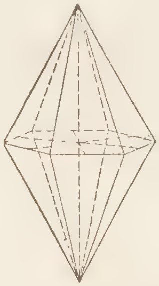


Fig. 31.—Hexagonal.

The properties of crystals differ when measured in different directions and they split in definite planes. Diamonds are crystalline, but the facets are cut to suit the lapidary and not in agreement with the natural form of that crystal. Sulfur as we learned has two crystal forms, and an energy change is involved in a change from one to the other. When a substance crystallizes in two systems it is *dimorphous* and two or more substances crystallizing in the same form are *isomorphous*. The crystal form is a valuable aid in the identification of substances. The sulfates of zinc, magnesium, and nickel crystallize with 7 H_2O to each molecule in almost exactly the same crystal form. Liquids may be cooled too rapidly to permit crystallization and in such cases glassy or gummy substances called "amorphous" solids result.

Exercise 7.—Concentrate some salt water and let it stand undisturbed in an open dish. To what system do these crystals belong? Examine good crystals of quartz, calcium carbonate, cane sugar (as seen in some fruit jellies or in rock candy), and copper sulfate, and name their crystal system.

Crystal Structure.—Diffraction gratings are made by ruling fine parallel lines on metal, glass, celluloid, etc. When these lines are separated by distances approximating the wave length of light a spectrum is produced by incident light similar to that formed by a common glass prism. Some gratings are marked with twenty-five thousand lines to the inch (one thousand to the millimeter).

It occurred to Laue in 1912 that if these parallel lines were closer together, separated by distances of the order of X-ray wave lengths, it should be possible to secure X-ray spectra similar to those with visible light. Now the waves in the ether known as X-rays are about one ten-thousandth the length of light waves. To make a grating for this effect there should be ruled nearly one hundred million lines to the inch, an impossibility. Laue found such gratings already prepared in crystal surfaces. Here, as Bragg pointed out in 1914, the atoms are arranged in a geometric pattern or lattice, giving the necessary parallel lines close enough together for Laue's needs.

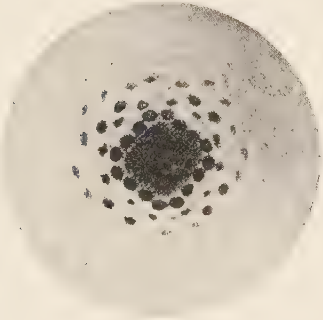


Fig. 32.—X-ray photograph of a crystal of zinc sulfide.

The lattice units are not single atoms in all cases. The familiar groups or radicals are found in some crystalline salts. In calcite crystals, $CaCO_3$, it was shown by X-ray examination that each carbon atom is surrounded by three oxygen atoms. The lattice unit of many carbon compounds (organic compounds) is the molecule as in frozen benzene where the lattice unit is C_6H_6. Even in crystals of salt-like solids the molecule is potential.

Figure 32 is a photograph made by the diffraction of a fine beam of X-rays in passing through a thin crystal of zinc sulfide to a photographic plate. Bragg explains that each spot is due to the regular reflection of the beam of X-rays from a plane in the crystal which is especially rich in atoms. It was found that in the diamond each carbon atom is surrounded by four others, so as to form a regular tetrahedron.

The simplest arrangement of atoms possible in a crystal is the system of equal closely packed cubes with atoms occupying the corners. This is characteristic of salts yielding an equal number of positive and negative ions (NaCl, for example).

The commonest system is the face-centered (Fig. 34) with atoms at the corners of a system of equal closely packed cubes and also at the centers of each cube face.

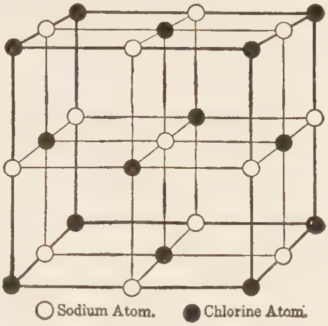
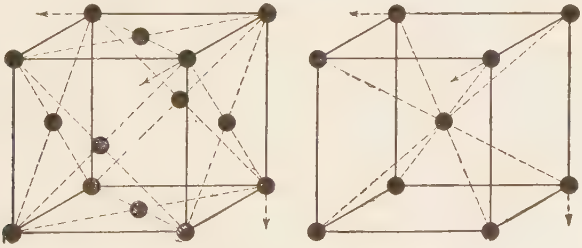


Fig. 33.—Cubic arrangement of atoms in a crystal of sodium chloride.

Wyckoff[1] states that X-ray analysis has so far shown that:

1. There is no metal crystallizing in the face-centered system which is not ductile throughout a considerable range of temperature.
2. All noble metals are in the face-centered system.
3. All the best conductors of heat and electricity are in the face-centered system.

Structure of Glasses.—X-ray study finds the same type of diffraction pattern for glasses as for liquids, in other words glasses and liquids are alike in their random, haphazard arrangement of molecules or other units. Crystals possess rigidity and a definite orderly structure, while glasses possess rigidity but a random arrangement of structural units.



Face-centered cube *Body-centered cube*

Fig. 34.—Arrangement of atoms in crystals.

Catalyst Lattice.—Irregular placement of atoms at the crystal surface above the normal surface of a solid catalyst may aid reactions by exposing more affinities, making the projecting atoms more unsaturated and active. For example the surface of a nickel catalyst may be represented thus:

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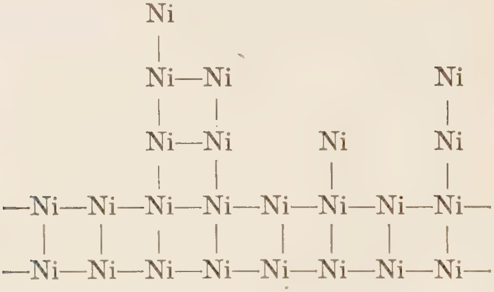
[1] *Structure of Crystals*, Chemical Catalog Co.



EXERCISES

8. A given quantity of gas has a volume of 15 liters at 740 mm. On coördinate paper plot a curve showing the application of Boyle's law when the pressure is changed to 150 mm., 200 mm., 250 mm., 300 mm., and 500 mm.

9. A liter of oxygen at 760 mm. is forced into a vessel containing a liter of nitrogen at 760 mm. What will be the resulting pressure?

10. How much heat is required to convert 100 g. of solid aluminum at its melting point into liquid aluminum at the same temperature?

11. When 150 g. of steam at 100° condense, cool to 0°, and freeze to ice, what is the total amount of heat liberated?

12. Could you use water instead of mercury in a barometer?

13. How would a tungsten lamp work at 1.7° absolute?

14. If a liter of gas were heated in a strong container, what would happen as the temperature rose 1° C.? The gas could not expand by 1/273 in accordance with Charles' law, yet the rise in temperature is accompanied by greater kinetic energy of the molecules.

15. Suppose an odorous gas, lighter than air, were released near the ceiling of a quiet room, would you ever smell it near the floor?

16. What is the kinetic theory of gases?

17. Why is so much energy required to change water at 100° C. into steam at 100° C.?

18. Define melting point and boiling point.

19. How are gases liquefied?

20. To what temperature must an open liter vessel be heated in order to drive out half of the molecules contained at 25° C.?

21. The density of gases is referred to oxygen, hydrogen, or air. If air is taken as a standard (density of 1) what is the relative density of carbon dioxide? One liter of air weighs 1.293 g. and one liter of carbon dioxide weighs 1.976 g.

22. Convert 25 cc. of a dry gas at 30° C. and 740 mm. to its volume at 10° C. and 700 mm.

23. A gas collected over water at 18° C. has a volume of 150 cc. when the pressure is 745 mm. What would be the volume of the dry gas at 0° C., 760 mm.? (The partial pressure of water vapor over water at 18° is 15.4 mm.)

24. The volume of a given sample of gas at 752 mm. and 9° C. is 38 cc. What will be its pressure when its volume is 20 cc. and its temperature 18° C.?

✓25. The volume of a given sample of gas at 800 mm. and 23° C. is 220 cc. The pressure is reduced to 600 mm. At what temp. would the gas occupy its original volume under this new pressure?

26. A gas occupies a volume of 30 cc. when measured over water at 20° C. and 745 mm. What volume will it occupy, dry at standard conditions?

27. Define critical temperature, absolute zero, associated molecules, fractional distillation, surface tension, viscosity, freezing point, heat of fusion.

28. On coördinate paper plot the Centigrade scale from − 40° C. to 100° C. on one axis and the Fahrenheit scale from − 40° F. (curiously enough, identical with − 40° C.) to 212° F. on the other axis. Complete the square and draw a heavy line from the origin (− 40°) diagonally to the opposite corner. By reading intersections on this "curve" convert any temperature on one scale into its equivalent on the other.

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CHAPTER VI

HYDROGEN

History.—The discovery of hydrogen should be credited to Turquet de Mayerne (1650), who treated iron with dilute sulfuric acid. He recognized the "inflammable air" formed as a distinct substance. Paracelsus had really done the same thing a century earlier but failed to recognize it as a distinct substance. Cavendish in 1766 discovered many of its properties. Lavoisier named it "Hydrogen," meaning "water former," although it was Cavendish who burned hydrogen in oxygen and proved that water is composed of hydrogen and oxygen.

Occurrence.—Hydrogen does not occur free in nature except for traces in the air (1 part in 10,000) and in natural gas and a considerable amount in gases erupted by very violent volcanic outbursts. All this is negligible. But in the combined form it is found in water, plant and animal tissues, petroleum, asphalt, and natural gas. Among laboratory reagents we learn that it is an essential element of all acids and bases.

Gigantic flames of incandescent hydrogen 300,000 miles high and 100,000 miles wide have been known to burst from the sun's chromosphere.

Preparation.—1. *Metals and Acids.* Since hydrogen is a constituent of such common materials as water, acids, and bases, these must be convenient sources for its preparation. In the laboratory it is extremely convenient to displace hydrogen from dilute acids by the more active metals. The hydrogen is collected by displacement of water.

$$\begin{aligned}
Zn + 2\,HCl &\longrightarrow H_2 + ZnCl_2, \text{ zinc chloride,}\\
Zn + H_2SO_4 &\longrightarrow H_2 + ZnSO_4, \text{ zinc sulfate,}\\
2\,Al + 3\,H_2SO_4 &\longrightarrow 3\,H_2 + Al_2(SO_4)_3, \text{ aluminum sulfate,}\\
2\,Al + 6\,HCl &\longrightarrow 3\,H_2 + 2\,AlCl_3, \text{ aluminum chloride.}
\end{aligned}$$

When a metal displaces hydrogen from an acid a ***salt*** is always formed. With hydrochloric acid this salt is called a "chloride," hence $ZnCl_2$ is zinc chloride and NaCl is sodium chloride (common salt). With sulfuric acid the salts are called "sulfates," with nitric acid the salts are called "nitrates" and with phosphoric acid the salts are called "phosphates." The less active metals, such as copper, mercury, platinum, gold, and silver, do not displace hydrogen from acids. Some acids react more readily than others for reasons to be developed later. Pulverized metals, naturally react more rapidly than do masses of metal because the greater surface allows better contact. A strip of very pure zinc is not attacked by dilute sulfuric, but if a less active metal, such as copper, is dropped in the acid and placed in contact with the zinc, hydrogen is released rapidly on the surface of the copper, although it is the zinc that is really attacked. The two metals form an electric "couple." Impurities in commercial zinc form many small local couples which make it react readily with acid.

2. *Metals and Bases.* Several active metals displace hydrogen from bases. In some cases a warm, 10 per cent solution of the base is used; in others the powdered dry metal and base are heated together:

$$Zn + 2\ NaOH \longrightarrow Na_2ZnO_2 + H_2,$$
$$2\ Al + 6\ NaOH \longrightarrow 2\ Na_3AlO_3 + 3\ H_2.$$

The first product is called sodium zincate and the second sodium aluminate.

By a "10 per cent solution" we mean a solution containing 10 grams of the dissolved substance to 90 grams (or cc.) of water. Of course other weights in the same proportions may be used.

It is sometimes found convenient but not economical to generate hydrogen by heating the non-metals silicon or boron with concentrated solutions of sodium hydroxide.

$$Si + 4\ NaOH \longrightarrow Si(OH)_4 + 2\ H_2.$$

3. *Metals and Water.* The most active metals, such as potassium and sodium, violently displace hydrogen from cold water. In fact a bit of such a metal the size of a pea is adequate for the experiment. It is well to take due precautions for the hydrogen is often ignited from the heat of reaction:

$$2\ K + 2\ H_2O \longrightarrow 2\ KOH + H_2,$$
$$2\ Na + 2\ H_2O \longrightarrow 2\ NaOH + H_2,$$
$$Ca + 2\ H_2O \longrightarrow Ca(OH)_2 + H_2.$$

An alloy of 65 per cent lead and 35 per cent sodium called "Hydrone" reacts rapidly but safely with water. The lead merely dilutes the sodium. An alloy of mercury and sodium (an amalgam) is also a safe hydrogen former for similar reasons. Calcium acts at moderate speed. In all cases the products are hydroxides of the metals used, sodium hydroxide, NaOH, for example. It is to be noted that only half the hydrogen in each molecule of water is displaced, unless the temperature is raised considerably, no matter how much metal is used.

EXERCISE 1.—From the topic "Metals and Bases" could you learn how to displace the remaining half of the hydrogen from water?

EXERCISE 2.—Lithium, although not a common metal, is nearly as active as sodium. Represent by an equation its reaction with water.

Less active metals react with water only when heated. Magnesium displaces hydrogen from boiling water if a little of a magnesium salt is present to keep the surface of the metal clean. Steam passed over red-hot iron reacts as follows:

$$3\ Fe + 4\ H_2O \longrightarrow Fe_3O_4 + 4\ H_2.$$

This is one of the great commercial methods of obtaining hydrogen. At such high temperatures as are used the oxides form because any possible hydroxides would be decomposed into oxides and water.

4. Electrolysis. When a current of electricity is passed through water, made conducting by the presence of some substance such as sulfuric acid or sodium hydroxide, we are able to collect two volumes of hydrogen at the cathode to one of oxygen at the anode (Fig. 35). Since this is the exact proportion in which they unite to form water on burning, the experiment adds convincing proof to our ideas on the composition of water. A detailed explanation of the action of the dissolved acid or base will be given under "Ionization." Yet it may be stated now that a small amount of sulfuric acid or sodium hydroxide for example,

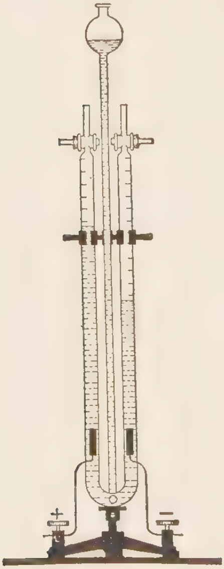

FIG. 35.—Electrolysis of water.

enables us to decompose an unlimited amount of water. Is the water a catalyst in this case?

A considerable amount of hydrogen has been secured as a by-product in the electrolysis of salt water. Here sodium chloride ($NaCl$) is decomposed to form chlorine gas (useful in bleaching and sterilizing) and sodium, which reacts with the water present to yield sodium hydroxide and hydrogen.

NOTE: A preliminary definition of acids, bases, and salts is now in order. An acid in water solution tastes sour, turns litmus paper red, and yields hydrogen when treated with the more active metals. A base in water solution feels soapy, turns litmus blue, and neutralizes the sour taste and other characteristic properties of an acid. Acids all contain hydrogen replaceable by a metal and bases all contain —OH groups attached to a metal. A salt is one of the products formed when a metal displaces hydrogen from an acid (the other being hydrogen) or when an acid and a base react (the other being water).

In the United States alone more than 300,000,000 lbs. of liquid fats are annually "hardened" or hydrogenated by the catalyzed addition of hydrogen. This equivalent of the fat from 7,000,000 hogs enormously increases the production of hard soap.

5. The Water Gas Methods. "Water gas" is essential to three commercial methods of making hydrogen. Water gas itself is prepared by passing steam over coke at about 1000° C.

$$C + H_2O \longrightarrow CO + H_2.$$

Of course, the coke is soon cooled by the steam below the reaction temperature. Steam is then shut off and a blast of air turned on. Part of the coke burns, heating the remainder up to 1000° C., and preparing it for another blast of steam.

By the *Liquefaction Process* this water gas (or mixture of carbon monoxide and hydrogen) is cooled to about $-200°$ C. and a pressure of twenty atmospheres applied. The carbon monoxide and some impurities liquefy, while the hydrogen is removed as a gas, since it cannot be liquefied above $-234°$ C., its critical temperature.

Another method promising great efficiency is the Water-Gas *Catalytic Process.* Water gas ($H_2 + CO$) and steam are passed over a catalytic mixture of the oxides of iron, chromium, and thorium at 500° C.

$$H_2 + CO + H_2O \longrightarrow 2\,H_2 + CO_2.$$

The steam oxidizes the carbon monoxide. The mixed gases are bubbled under pressure through water, which takes out the carbon dioxide. This is a continuous process and very economical.

The Steam-Iron Process, although its position is threatened, still furnishes much of the world's hydrogen. Steam is passed over red-hot iron:

$$3\,Fe + 4\,H_2O \longrightarrow Fe_3O_4 + 4\,H_2.$$

As soon as the reaction ceases, because of the formation of a protecting film of oxide, water gas is turned on for twenty minutes:

$$Fe_3O_4 + 4\,H_2 \longrightarrow 3\,Fe + 4\,H_2O,$$
$$Fe_3O_4 + 4\,CO \longrightarrow 3\,Fe + 4\,CO_2.$$

The water gas is then shut off, more steam turned on for ten minutes, and more hydrogen thus produced. By alternate use of steam and water gas the same mass of iron is used indefinitely. The electrolytic process is used to some extent commercially. It produces a very pure hydrogen. If a solution of sulfuric acid is used, the electrodes should be of lead; if a solution of sodium hydroxide is used, iron electrodes can be used without attack by the liquid. The demand for oxygen, a by-product in this case, helps to reduce the cost of hydrogen.

6. Modern development of the ***Hydrocarbon Process*** for making hydrogen is worthy of note. Any compound of hydrogen and carbon may be broken down or "cracked" into its elements if sufficiently heated without access of air. A layer of burning coke is preheated by a blast of air to 1300° C., and the "blast gas" so formed is burned in a tower partly filled with a checker work of fire brick (the vaporizer). When both coke and vaporizer are hot enough oil is sprayed on the hot brick work, and the resulting vapors passed over the hot coke, where they are cracked into hydrogen and carbon.

The carbon deposited on the coke is burned by the next air blast.

One company cracking natural gas for the carbon (a valuable form called "carbon black") wastes 10,000,000 cubic feet of hydrogen daily.

The ***coke oven gas*** made from one ton of bituminous coal contains about twenty-seven pounds of free hydrogen. This is a commercial source wherever the price is very low, as it is in Europe.

Purification of Hydrogen.—The zinc, iron, or other metals used in the preparation of hydrogen usually contain impurities that form offensive hydrogen compounds. To purify the gas it is first bubbled through water to catch any spray of droplets of the generating solution. All gases coming out of a liquid carry a spray just as do winds from the ocean waves. A loose wad of cotton is often used to hold the droplets. Next the gas is passed through a dilute alkaline solution of potassium permanganate, a compound which readily gives up its oxygen to substances capable of taking it on. In other words, potassium permanganate oxidizes the impurities into compounds retained by the solution while the hydrogen passes on unchanged and may be dried by a tube of anhydrous calcium chloride.

If the hydrogen is generated in direct contact with the oxidizing agent, for example by putting zinc, acid, and permanganate all in the same tube, much of the hydrogen unites with the oxygen of the permanganate to form water. The solution is decolorized, yet if pure hydrogen from another vessel is passed through a solution of permanganate, there is no loss of color.

Hydrogen absorbed by certain finely divided metals is very active. Absorbed by spongy palladium it reduces nitrates to ammonia. Perhaps the electron orbits in some of the molecules or atoms are disturbed by contact with the metal. Even common zinc as it displaces the hydrogen from acids may activate the hydrogen by surface influence.

Physical Properties.—Hydrogen is a colorless, odorless, tasteless gas. A liter weighs 0.08987 g. at standard conditions, so it is the lightest substance known. Liquid hydrogen looks like water, but a cork sinks in it as quickly as does a stone in water. The gas may be poured upward from cylinder to cylinder. At ordinary temperatures and 760 mm. pressure 2 cc. will dissolve in 100 cc. of water. It cannot be liquefied above −234° C., its critical temperature. It has been frozen at −259° C., into a transparent, ice-like solid. Powdered palladium under favorable conditions has absorbed 900 times its own volume of hydrogen, and such absorbed hydrogen is very reactive chemically. This property of dissolving in metals probably explains in part why hydrogen passes through thin sheets of hot gold, platinum, and other metals. Of course, as indicated by Graham's law, it has the greatest speed of diffusion of all gases, and this is another factor. The loss by diffusion through balloon fabric is a serious problem.

Exercise 3.—A balloon is inflated near the ground. At a great height it expands, since the air pressure around it is less. Will the leakage by diffusion change?

When a large beaker of hydrogen is placed over a porous cup, connected as in Figure 36, a jet of water is forced out of the tube like a fountain. Hydrogen diffuses into the cup faster than air diffuses out, hence pressure is developed.

When hydrogen is inhaled (great danger of a fatal explosion if a flame is near!) the bass voice becomes tenor or even falsetto. The pitch of organ pipes and other wind instruments is also raised when a blast of hydrogen is used instead of air because the vibration frequency varies inversely as the square root of the density of the gas employed.

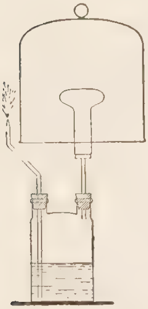

Fig. 36.—A hydrogen diffusion fountain.

Para Hydrogen.—In 1929 the German chemist, Bonhoeffer, showed that ordinary hydrogen is a mixture of the ortho and para forms in the ratio of about 75 per cent to 25 per cent and that at the temperature of liquid hydrogen, using charcoal as a catalyst to convert one form into the other, we can secure 99.7 per cent pure para hydrogen. The spectra and the specific heats of these two forms of hydrogen are quite distinct and they can be easily recognized. These two forms of hydrogen are both composed of molecules of hydrogen having two atoms per molecule; they differ in that in one form the nuclei of the atoms are rotating in the same direction, while in the other form, the nuclei are rotating in opposite directions.

Chemical Properties.—Hydrogen is rather inactive at ordinary temperatures, but at higher temperatures unites with most of the non-metals and many of the metals:

$$S + H_2 \longrightarrow H_2S,$$
$$Cl_2 + H_2 \longrightarrow 2\ HCl,$$
$$O_2 + 2\ H_2 \longrightarrow 2\ H_2O,$$
$$N_2 + 3\ H_2 \longrightarrow 2\ NH_3.$$

Hydrogen unites with hot sulfur vapors at 250° to form the offensive gas, hydrogen sulfide. With chlorine gas it reacts when hot to form hydrogen chloride (which in water solution is hydrochloric acid). A jet of hydrogen, or even illuminating gas, burns in a jar of chlorine just as truly as it burns in a jar of oxygen. A mixture of chlorine and hydrogen can be exploded by a bright light. The Haber process of uniting hydrogen with nitrogen to form ammonia was mentioned as of tremendous importance in the recent war.

Hydrides.—Since compounds of oxygen with one other element are termed oxides it is logical to refer to compounds of hydrogen with one other element as ***hydrides.*** Water is not only an oxide but a hydride and ammonia is nitrogen hydride.

Most non-metals form hydrides, rather stable in general, while only a limited number of the metals form hydrides, comparatively unstable. The metallic hydrides of the more active metals are formed by merely heating the metal in hydrogen. They react with water to form hydrogen.

$$NaH + H_2O \rightarrow H_2 + NaOH,$$
$$CaH_2 + 2H_2O \rightarrow 2H_2 + Ca(OH)_2.$$

The hydrogen flame is intensely hot, as 34,195 calories are released when one gram of hydrogen burns. That water is formed can be shown by holding a cold, dry beaker above the flame. Drops of moisture condense on the glass. The hydrogen may be purified by contact with a solution of potassium permanganate and drying over anhydrous calcium chloride. A great deal of heat is wasted when hydrogen burns in air. Not only does the nitrogen interfere with good contact between the reacting elements but it cools the flame by absorbing heat. That is why a flame can be "blown out" by the cooling effect of too much air. A special burner, called the oxyhydrogen blowpipe (Fig. 37), was devised by the pioneer American chemist, Robert Hare. This device insures proper mixing of a stream of oxygen and a stream of hydrogen. In this flame platinum melts and silver boils. The temperature ranges from 1800° C. to 2500° C., as conditions vary. Hydrogen burns with a colorless flame unless a glass tip or something of the sort is used. Then the sodium compounds in the glass color the flame yellow.

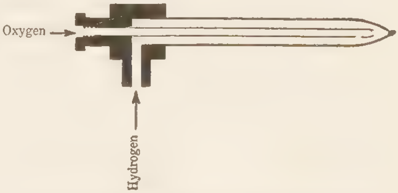

FIG. 37.—Oxyhydrogen blowpipe.

The reaction between oxygen and hydrogen is negligible at room temperature; a noticeable amount reacts in a few hours at 518° C.; at 600° C. the reaction is rapid; and at 700° explosive. This means that it requires a flame or red-hot solid to ignite the mixture. Platinum, finely divided, catalytically speeds up the trifling reaction at ordinary temperatures to a point where it becomes incandescent with the heat evolved. It then ignites the mixture. Gas lighters make use of this principle.

Morley of Western Reserve University spent years of marvelously accurate work in ascertaining the exact weights of hydrogen and oxygen combining to form water. His results, the most accurate known, indicate that 1 part by weight of hydrogen unites with 7.94 parts of oxygen. Long before Morley's time it was known that two volumes of hydrogen unite with one volume of oxygen to form two volumes of water (as vapor).

This interesting ratio, and many others, led Gay-Lussac to state that ***whenever in any chemical reaction gases appear or disappear they do so in the ratios of small whole numbers by volume*** (Gay-Lussac's Law).

Hydrogen, when hot, removes oxygen and even some other elements from many compounds. Such a process is called ***reduction,*** the exact opposite of ***oxidation.*** However a broader conception of reduction will soon be presented. Figure 4 (page 12) represents the reduction of heated copper oxide by dried hydrogen. The water formed is taken up by the calcium chloride in the U tube:

$$CuO + H_2 \longrightarrow Cu + H_2O.$$

The temperature of reduction of black copper oxide by hydrogen ranges from about 90° (if the oxide has been prepared from copper hydroxide, washed, and dried at 130°) to 205° for the reduction of oxide made by heating copper nitrate. Furthermore if the reduced metal powder is again oxidized in a stream of heated oxygen (or air) the temperature of later reduction is lowered. By repeating this procedure a few times a copper oxide reducible by hydrogen at 100° is readily obtained.

Reversible Reactions.—The mysterious attraction that holds elements together is sometimes called ***chemical affinity.*** When hot hydrogen ***reduces*** some metallic oxide, that is, steals oxygen away, we are tempted to say that this occurs because hydrogen has a greater affinity for oxygen than has the metal. Consider iron oxide, for example:

$$(1) \quad Fe_3O_4 + 4\,H_2 \longrightarrow 3\,Fe + 4\,H_2O.$$

A stream of hydrogen passed over the hot oxide reduces it to the metal by stealing the oxygen. Apparently iron does not have the force to hold its own. If through the same tube we pass a current of steam (Fig. 38), the following reaction occurs:

$$(2) \quad 3\,Fe + 4\,H_2O \longrightarrow Fe_3O_4 + 4\,H_2.$$

The steam oxidizes the iron back to the oxide, leading us to the conclusion that iron removes the oxygen from steam because it has a greater affinity for oxygen than has hydrogen. But here are two conflicting conclusions. Both cannot be true. Now if we seal iron and water in a strong closed tube and heat it for a time, we find on opening the tube all four substances,—iron, hydrogen, steam, and iron oxide. Evidently when the products of reaction could not escape both reactions took place. We express the facts thus:

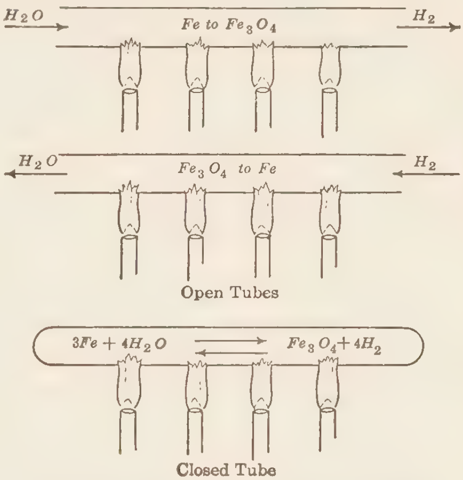

FIG. 38.—Reactions in open and closed tubes.

$$(3) \quad Fe_3O_4 + 4\,H_2 \rightleftarrows 3\,Fe + 4\,H_2O,$$

and call it a ***reversible reaction.*** In equation (1) the steady flow of hydrogen swept the steam out of the tube before it had a fair chance to react with the iron. In equation (2) the steady flow of steam swept the hydrogen out of the tube before it had a fair chance to react with the oxide. But in a closed tube every possible reaction has a chance because nothing escapes; the four substances remain in good contact. It appears, then, that chemical affinity alone is not sufficient to explain all reactions. The conditions of reaction are important. Many reversible reactions can be made to proceed to completion by any device for removing one of the products or turning it into something inactive. The escape of a gas or the formation of an insoluble precipitate prevents reversal. There is comparatively little contact with precipitates. Some reactions are not reversed even if good contact is secured. An example follows:

$$2\ KClO_3 \longrightarrow 2\ KCl + 3\ O_2.$$

In any reversible reaction like that represented by equation (3) the two opposing reactions adjust their speeds until equal; and a condition of ***equilibrium*** is reached when there is no further change in the relative quantities of the reacting substances. Of course any change in the conditions such as temperature, etc., will disturb this equilibrium to the right or left by favoring one reaction more than the other. A new equilibrium is soon reached. For example, in a sealed tube containing iron and water when equilibrium is reached at 200° there are twenty volumes of steam to one of hydrogen, but at 440° only six volumes of steam to one of hydrogen, and at 1500° the volumes are equal.

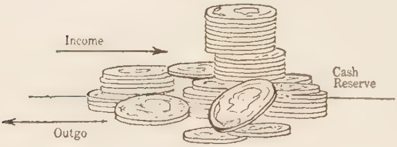

Fig. 39.—Financial Equilibrium.

To make the idea of equilibrium clear by the use of a rather informal illustration, let us consider the financial status of the average college student. He begins the year with a reasonable cash reserve for emergencies, a regular allowance from home, and the expectation of certain steady expenditures, some necessary and others in the luxury class. If we consider Income and Expenditure (Outgo) as analogous to two opposing chemical reactions and the Cash Reserve as an amount that may grow, decrease, or remain fixed (constant) as the relative velocities of Income and Outgo vary, we have a useful parallel. A healthy condition of financial equilibrium seems desirable.

Exercise 4.—Is the manufacture of ozone an example of a reversible reaction?

Exercise 5.—Why does the reaction between iron and hydrochloric acid proceed to completion although under proper conditions hydrogen reacts with the ferrous chloride formed?

$$Fe + 2HCl \rightarrow FeCl_2 + H_2.$$

Exercise 6.—Remembering that liquid water turns into gaseous water, that is, evaporates, give the equilibrium discussion as applied to a stoppered bottle partly filled with water.

When the stopper is removed, what happens?

Uses of Hydrogen.—Hydrogen manufacture is no longer a negligible industry. For many years this gas has been used in the oxyhydrogen blowpipe to weld metals or cut up large masses of scrap iron. As mentioned before, it has a large and growing use in hardening fats. Cottonseed oil, for example, is a liquid fat, but if hydrogen under seventy pounds pressure is passed through it in the presence of finely divided nickel (at 175° C.), the hydrogen adds directly to the fat molecules, forming a new substance, also a fat, but a solid. "Crisco," "Snowdrift," and similar substitutes for lard in cooking, are made in this way. From 500 to 5000 cubic feet of hydrogen react with one ton of fat. Some liquid fats are decomposed to yield liquid acids which are hardened by hydrogenation to form solids suitable for use in candles. Liquid fats are also hardened for use in soap making.

Hydrogen is also used in the reduction of tungsten from its ores and in the manufacture of ammonia by direct union of nitrogen and hydrogen (Haber process). Since ammonia is a starting point in the manufacture of fertilizers and of explosives this insures a great and growing demand for hydrogen.

The use of hydrogen in balloons and airships continues as a peace enterprise. One liter of hydrogen weighs 0.09 g., but one liter of air weighs 1.29 g. Hence the lifting power of a liter of hydrogen is the difference, or 1.2 g. under ordinary conditions.

EXERCISE 7.—The new airships for the United States Navy will hold 6,500,000 cubic feet of gas. Calculate their lifting power from the buoyant effect of a liter, as just given. In the Appendix is a table giving the number of liters in a cubic foot. These airships will be 785 feet long and 133 feet in diameter.

Atomic Hydrogen.—Palladium powder absorbs nine hundred times its own volume of hydrogen and in so doing seems to activate the hydrogen. At any rate, in such a condition hydrogen reduces, at room temperature, nitric acid, ferric chloride, and other substances not reduced at all by common hydrogen gas. In all probability the hydrogen acts like a metal, displacing from their salt solutions less active metals like silver, gold, platinum, probably because it is in the more active atomic condition.

Even a film of hydrogen gas adsorbed on the surfaces of very porous silica (SiO_2) has this same property of precipitating the least active metals from solutions of their salts. If the hydrogen molecules in contact with the silica surface have not actually been separated into atoms the attractive forces between these atoms must at least be seriously weakened, thus making the molecules active.

Wood made atomic hydrogen by a high-tension electric discharge through moist hydrogen. He thought that a film of water covered the glass walls and prevented the glass from catalyzing the transition of atomic hydrogen to the molecular form.

Langmuir made atomic hydrogen by heating filaments of tungsten, palladium and platinum to a high temperature in low-pressure hydrogen. Thus activated, this hydrogen after being cooled to room temperature combined directly with oxygen.

The Atomic Hydrogen Flame.—Langmuir passed a stream of hydrogen through an electric arc formed between tungsten electrodes and secured a temperature far above that of the oxyhydrogen flame. The electric energy of the arc decomposed the hydrogen molecules into atoms which united again with release of a very great amount of heat. The inner flame consists of atomic hydrogen burning in molecular hydrogen while surrounding this is a flame of molecular hydrogen burning in air. A tungsten wire with the very high melting point of 3400° C. drips like an icicle in the tip of the inner flame.

$$2\,H \rightleftharpoons H_2 + 90{,}000 \text{ cal.}$$

This flame is especially suited to certain types of welding.

The Activity Series of Metals.—We have already noted that sodium and potassium violently displace hydrogen from cold water, that calcium does so at moderate speed, that magnesium reacts noticeably with boiling water, that red-hot iron reacts with steam, and that copper and platinum do not react with water under any conditions. We have also noticed that magnesium and aluminum displace hydrogen from a dilute acid with much greater speed than does zinc or iron. Furthermore we have learned that copper and gold and platinum do not displace hydrogen at all from acids. These, and other facts, enable us to write the metals in the order of their activity, the most active at the top.

Potassium
Sodium
Barium
Strontium
Calcium
Magnesium
Aluminum
Manganese
Zinc
Cadmium
Iron
Nickel
Tin
Lead
Hydrogen
Copper
Mercury
Silver
Platinum
Gold

Silver and the metals below it do not unite directly with oxygen, but the farther above silver a metal is, the more vigorously it unites with oxygen. Since the metals below hydrogen do not displace hydrogen from the carbonic acid of natural waters, they are the only ones found free as minerals. The higher in the series a metal is placed (calling potassium "high") the more difficult it is to reduce its oxide with hot hydrogen. This means that the more active elements form the more stable compounds. For example, the oxides of the "noble" metals, such as mercury, are unstable on heating.

How to Solve Problems.—Suppose we solve a problem as an example of an almost infallible method.

How many grams of hydrogen are formed when 80 grams of zinc react with sufficient hydrochloric acid to dissolve the metal?

I. Write the equation:

$$\mathrm{Zn} + 2\,\mathrm{HCl} \longrightarrow \mathrm{H_2} + \mathrm{ZnCl_2}.$$

II. Select the two substances that are being discussed. From the equation we learn how many atoms or molecules are being compared.

$$\mathrm{Zn}\begin{cases} \\ \\ \end{cases}$$

$$2\,\mathrm{H}\begin{cases} \\ \\ \end{cases}$$

(We balanced the equation solely to learn that one atom of zinc and two atoms of hydrogen are being compared. We are not concerned with the amount of HCl provided there is enough to react with all the Zn, nor does the problem ask anything about the $\mathrm{ZnCl_2}$.)

III. Write down four numerical values, two in grams, etc., and two in terms of atomic weights. Or course, the value to be found is x grams, etc.

$$\mathrm{Zn}\begin{cases} 80\text{ g.} \\ \\ 65.38 \end{cases}$$

$$2\,\mathrm{H}\begin{cases} x\text{ g.} \\ \\ 2.01 \end{cases}$$

(A common error here is to write down the atomic (or molecular) weights of the two substances, but note that we are comparing the weights of *one* atom of zinc and *two* atoms of hydrogen.)

IV. Write these four values in a chemical proportion. Any value will do for the first term, but the first and second must use the same units as grams-grams or atomic weights-atomic weights, while the first and third terms must refer to the same substance. Label the terms and solve for x.

$$\begin{aligned} \text{g. of Zinc} : \text{g. of Hydrogen} &= \text{Wt. of Zn} : \text{Wt. of 2 H}, \\ 80 : x &= 65.38 : 2.01, \\ x &= 2.46 \text{ grams of hydrogen.} \end{aligned}$$

If this method is followed closely, mistakes will be rare. Had liters of hydrogen been asked for, the 2.46 g. could be converted into liters after learning the weight of one liter.

Optional Method of Solving Problems.—Suppose we wish to learn how many grams of zinc will be required to displace 200 grams of hydrogen from hydrochloric acid.

$$\underset{65.38}{Zn} + 2\,HCl \longrightarrow ZnCl_2 + \underset{2.016}{H_2}.$$

It is evident from the above balanced equation that 65.38 g. of zinc displace 2.016 g. of hydrogen. Therefore to displace 1 g. of hydrogen $\frac{65.38}{2.016}$ g. of zinc will be required and to displace 200 g. there must be used $200 \times \frac{65.38}{2.016}$ g. $= 6486$ g. of zinc.

Suppose we wished to prepare 50 g. of oxygen from potassium chlorate. How many grams of the chlorate must we heat?

$$\underset{245.12}{2\,KClO_3} \longrightarrow 2\,KCl + \underset{96}{3O_2}.$$

Clearly 245.12 g. of the chlorate yield 96 g. of oxygen, therefore to yield 1 g. of oxygen there will be needed $\frac{245.12}{96}$ g. of chlorate. To yield 50 g. of oxygen there must be heated $50 \times \frac{245.12}{96}$ g. $= 127.66$ g. of $KClO_3$.

The "Weight Factor" for the fraction of oxygen in any quantity of potassium chlorate is evident in the above calculation. Since 245.12 g. of potassium chlorate contains 96 g. of oxygen, 1 g. of the chlorate must contain $\frac{96}{245.12}$ g. $= 0.3916$ g. Therefore 0.3916 of any weight of the chlorate is oxygen. This weight factor, 0.3916, is conveniently used in calculations.

EXERCISES

8. How is a "salt" formed? Name a few.

9. What are the "water gas" methods of preparing hydrogen?

10. Outline the hydrocarbon process for making hydrogen.

11. Name four elements with which hydrogen unites directly on heating.

12. How is the oxyhydrogen blowpipe built? Why not use air in it?

13. If you heated potassium chlorate in a strong closed tube, would the reaction be reversible?

14. Invent a better illustration of equilibrium than the financial episode.

15. How can you change cottonseed oil ("Wesson oil") into a fat having the consistency of lard?

16. Calculate the "weight factor" of copper in $CuSO_4 \cdot 5\ H_2O$ (blue vitriol).

17. When a proper mixture of hydrogen and oxygen is ignited a sharp explosion occurs. The pressure generated may even burst the containing vessel. Since fewer molecules (of water vapor) exist than before,

$$2\ H_2 + O_2 \rightarrow 2\ H_2O,$$

how can you account for the increase in pressure?

18. Eleven liters of hydrogen are passed through a heated tube containing dry copper oxide. What weight of water could be condensed beyond the heated tube?

19. How many liters of hydrogen can be released from water by 80 g. of calcium?

20. How many grams of iron will be required to release 100 g. of hydrogen from sulfuric acid?

21. How many grams of sulfuric acid will exactly react with 48 grams of aluminum?

22. Compare hydrogen and oxygen in several properties.

23. Will silver react with hydrochloric acid?

24. Will gold rust or burn?

25. Calculate the percentage of oxygen in potassium chlorate.

26. How many grams of oxygen are in 1 Kg. of potassium chlorate?

27. What weight of 20 per cent sulfuric acid would be required to prepare 140 liters of hydrogen?

28. Hydrogen was passed over heated copper oxide. The water formed was collected and found to weigh 25 g. (a) What is the weight of the hydrogen that reacted with the copper oxide? (b) What is the loss in weight of the CuO?

29. What weight of zinc must be added to excess hydrochloric acid to produce 22.4 liters of hydrogen at 0° to 760 mm.?

30. Ten grams of water are (1) decomposed by sodium; (2) another 10 g. passed as steam over red-hot iron; (3) another 10 g. decomposed by an electric current. What volume of gas under standard conditions is produced in each case?

REFERENCES

"Some Reactions of Atomic Hydrogen" (Urey and Lavin), *Journal of the American Chemical Society*, *51*, 3286, (1929).

REVIEW SUGGESTIONS

Ten minutes' questioning of yourself on the things brought out in the lecture if given within two hours is worth an hour's review the next day.

In all equations underline the formulas for insoluble products. Use an arrow pointing upward (↑) to indicate the escape of gases formed.

In writing equations it tends toward clearness to "fence in" the elements that you know from laboratory observation must unite.

$$Cu\,\boxed{O + H_2} \rightarrow H_2O + Cu,$$

$$Fe_3\,\boxed{O_4 + 4\,H_2} \rightarrow 4\,H_2O + 3\,Fe.$$

Monday

CHAPTER VII

VALENCE

Valence is most easily understood by reasoning from experiment. If we weigh out the metals sodium, magnesium, and aluminum in proportion to their atomic weights, we should take 23 g. Na, 24 g. Mg, and 27 g. Al. For that matter 23 tons Na, 24 tons Mg, and 27 tons Al would maintain the same proportion. As a matter of convenience it is better to weigh out 23 mg. Na, etc.

It is of vital importance here to know that a "gram-atomic weight" of sodium (23 g.), a gram-atomic weight of magnesium (24 g.) and a gram-atomic weight of aluminum (27 g.) all contain the same number of atoms. If this is not clear, imagine that French soldiers average 150 lb. and German soldiers 160 lb. Calculate the number of soldiers in a detachment of Germans with a total weight of 160,000 lb. and in a detachment of French soldiers with a total weight of 150,000 lb. Evidently there are 1000 men in each detachment. We weighed out both groups in proportion to the weights of the individuals.

Suppose, then, that we weigh out 23 mg. of sodium, 24 mg.[1] magnesium, and 27 mg. of aluminum and introduce them under inverted tubes of dilute hydrochloric acid (a solution of HCl in water). After the hydrogen released has displaced water from the tubes into the beaker of water below, the tubes are adjusted until the levels of water inside and out are the same. Making the usual corrections for pressure, temperature, and presence of water vapor, the results are as follows:

23 mg. sodium release 11 cc. hydrogen = 1 mg.
24 mg. magnesium release 22 cc. hydrogen = 2 mg.
27 mg. aluminum release 33 cc. hydrogen = 3 mg.

(From the weight of 1000 cc. of hydrogen, 0.09 g., the weight of 11 cc. or any other volume can be calculated by proportion.)

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[1] In practice it is best to put the fresh-cut sodium in a small gelatin capsule. In a few minutes the capsule is dissolved and the water comes in contact with the sodium. Magnesium ribbon should be cleaned with sand-paper and aluminum etched with dilute base, washed, and dried before weighing.

From the above results we see that one atomic weight of sodium *in milligrams* released exactly one atomic weight of hydrogen in milligrams, while one atomic weight of magnesium in milligrams released *two* atomic weights of hydrogen in milligrams, and one atomic weight of aluminum in milligrams released *three* atomic weights of hydrogen in milligrams.

By using the *atomic weight* of each metal in milligrams we knew we were using equal numbers of atoms. The above results can then be expressed as:

1 atom of sodium displaces 1 atom of hydrogen.
1 atom of magnesium displaces 2 atoms of hydrogen.
1 atom of aluminum displaces 3 atoms of hydrogen.

$$\begin{aligned} Na + HCl &\longrightarrow NaCl + H, \\ Mg + 2\,HCl &\longrightarrow MgCl_2 + 2\,H, \\ Al + 3\,HCl &\longrightarrow AlCl_3 + 3\,H. \end{aligned}$$

Not merely does one atom of sodium displace one atom of hydrogen, but in the resulting compound, sodium chloride, it holds one atom of chlorine. To be sure that was just what one atom of hydrogen did in a molecule of hydrogen chloride (HCl). We see that the displacing capacity (towards hydrogen) and the holding capacity (towards chlorine) are twice as great with magnesium and three times as great with aluminum as with sodium. ***Valence, the capacity of an element to hold other elements in combination, is measured by the number of atoms of hydrogen or chlorine held by one atom of the given element.*** One atom of a monovalent element displaces or holds one atom of hydrogen or holds one atom of chlorine. Of course one atom of a divalent element could displace two atoms of hydrogen or hold two atoms of chlorine. Magnesium must be divalent and aluminum trivalent. Oxygen, as shown by the formula H_2O, must have a valence of two, since one atom holds two atoms of monovalent hydrogen. CaO is the accepted formula for quicklime, calcium oxide. Since we have just reasoned that the valence of oxygen is two, we now have a logical right to state that the valence of calcium is also two, for one atom of calcium holds one atom of divalent oxygen. A common error at this point is the incorrect statement that any *element* one atom of which holds just one atom of any other element is monovalent.

EXERCISE 1.—According to the formulas HCl, H_2O, NH_3, and CH_4, what do we know of the valence of chlorine, oxygen, nitrogen, and carbon?

We have just learned by experiment that the valence of aluminum is three. And since oxygen is divalent the correct formula for aluminum oxide must be Al_2O_3. The total valence of the two aluminum atoms is six, which equals, as it should, the total valence, six, of the three oxygen atoms.

EXERCISE 2.—What must be the correct formula of magnesium oxide? Of calcium chloride? Of sodium oxide?

It must be admitted that some elements have two or more valences, but most have only one. In red cuprous oxide, Cu_2O, the copper is monovalent, for it takes two atoms of it to hold one divalent oxygen atom. In black cupric oxide, CuO, the copper is divalent, for one atom holds one atom of divalent oxygen. In the two chlorides of iron, $FeCl_2$ and $FeCl_3$, ferrous and ferric chlorides, we have another illustration of variable valence. Nitrogen in its five oxides, N_2O, NO, N_2O_3, NO_2, N_2O_5, shows different valences. But when an element has more than one valence it is well to remember that in most cases only one is common. The usual valence of copper is two.

Radicals.—We have already noticed in equations such as

$$\begin{aligned} 2\,Na + H_2SO_4 &\longrightarrow Na_2SO_4 + H_2, \\ Mg + H_2SO_4 &\longrightarrow MgSO_4 + H_2, \\ 2\,Al + 3\,H_2SO_4 &\longrightarrow Al_2(SO_4)_3 + 3\,H_2, \\ BaCl_2 + Na_2SO_4 &\longrightarrow BaSO_4 + 2\,NaCl, \end{aligned}$$

that one sulfur atom and four oxygen atoms seem to hold together as a group or *radical* during reactions, passing from one compound to another unchanged, much as a family of Arabs might move from one tribe to another without the loss of any of its units, parents or children. We call the SO_4 group of atoms the "sulfate radical." It is incapable of existing alone and its compounds are always called "sulfates." For example, H_2SO_4 is always known as "sulfuric acid," but it could be called "hydrogen sulfate." Sodium sulfate is Na_2SO_4, magnesium sulfate is $MgSO_4$, and aluminum sulfate is $Al_2(SO_4)_3$. In nitric acid, HNO_3, and the nitrates derived from it such as $NaNO_3$ and $Cu(NO_3)_2$, we find the NO_3 group of atoms holding together pretty well through all sorts of reactions, so we call it the "nitrate radical." In phosphoric acid, H_3PO_4, and the phosphates made from it, such as Na_3PO_4, we see a similar group—PO_4—called the "phosphate radical." These radicals have valence. Thus in HNO_3 a single nitrate radical holds one monovalent hydrogen; in H_2SO_4 the sulfate radical plainly holds two hydrogens; in H_3PO_4 the phosphate radical holds three hydrogens. The natural assumption is that the nitrate radical is monovalent, the sulfate radical divalent, and the phosphate radical trivalent. We can easily learn the valence of any acid radical by looking up the correct formula of the corresponding acid and counting the hydrogen atoms held by one radical. A knowledge of the valence of radicals is very convenient in remembering correct formulas. For example, $CuSO_4$ must be the correct formula for copper sulfate (blue vitriol) because we know already that copper is divalent (see CuO) and so is the sulfate radical (see H_2SO_4). Therefore the two valences just exactly hold each other, as they should in all compounds. $Al_2(SO_4)_3$ must be the correct formula for aluminum sulfate because the valence of aluminum is three (see $AlCl_3$) and of the sulfate radical two. Consequently $AlSO_4$ cannot be right, because a valence of three for the metal is not equal to a valence of two for the radical. Two aluminum atoms furnish a total of six (2 × 3), just equaled by the total valence six (3 × 2) of the three sulfate radicals. It is a great help to put dots above the elements or radicals, as in $Ca''Cl_2$ or $Al_2'''(SO_4)_3''$ or $Cu''(NO_3)_2'$ to indicate their valence.

Valence Table

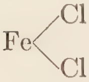
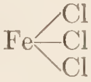
Monovalent		Divalent		Trivalent		Tetravalent
H	—OH	Mg	O	Al	—PO_4	C
Na	—NO_3	Ca	Fe	Fe	N	Si
K	NH_4—	Ba	Pb	Cr		
Cl	Br	Zn	—SO_4			
		Cu	—CO_3			

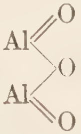
Exercise 3.—With the help of the above valence table write the correct formulas for sodium sulfate, zinc nitrate, cupric bromide, aluminum nitrate, aluminum hydroxide, carbon tetrachloride, carbon dioxide, silicon dioxide, barium sulfate, magnesium hydroxide, ferric chloride, and ferrous sulfate.

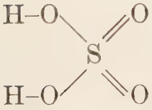
Exercise 4.—If 65.4 mg. of zinc displace 22 cc. of hydrogen from some acid, what must be the valence of zinc? Deduce this from the valence experiment at the beginning of the chapter.

EXERCISE 5.—Since CaO is the correct formula for calcium oxide (quicklime), what must be the formula for calcium bromide? Of calcium sulfate?

Structural Formula.—It is convenient to represent the valence attraction between elements by straight lines or "bonds of valence." Thus Na—Cl is the structural formula for sodium chloride (common salt). Since the valence of sodium as well as that of chlorine is one, this single line is a convenient picture of the relation.

 and  represent ferrous chloride and ferric chloride, in which iron is seen to have valences of two and three. The "-ic" compounds of a metal are those in which the metal has a higher valence than the "-ous" compounds.

The formula  merely represents Al_2O_3, showing the usual valences of three for aluminum and two for oxygen.

 is the structural formula for sulfuric acid. The memory need not be burdened with this at present. An annoying question that will not down in the student's mind is this: "What is the valence of the sulfur inside the $-SO_4$ radical?" And it is a further cause of disquiet that the student already knows that four oxygen atoms have a total valence of *eight*, yet he is told the valence of the whole group is only *two!*

A glance at the structural formula of sulfuric acid shows us that the sulfur atom and the four oxygen atoms of the SO_4 radical are well occupied in holding each other. Their effective outside valence toward hydrogen or other atoms is only two.

Group valence is paralleled by the effectiveness of a group of ten skaters attempting to rescue a comrade who has unfortunately broken through thin ice some distance from shore. The ten join hands to form a rescue chain with a single hand at one end grasping a tree for anchorage and a single hand at the other end reaching out to the sinking victim. Although the ten have a total of twenty hands (valence bonds?) all but one are occupied in holding the individuals of the group together and to the tree. The effective group valence is only one.

Positive and Negative Valence.—Discoveries of the last third of a century have proved that the atom is not a simple unit. The neutral atom is a miniature solar system, made up of positive charges of electricity (protons) at the center, and mixed with and surrounding these an equal number of negative charges of electricity (electrons).

When sodium unites with chlorine to form molecules of sodium chloride, the sodium atom really loses an electron to the chlorine atom. This leaves an excess of *one* positive charge on the sodium atom—and in the compound formed the valence of the sodium atom is *one*, a positive valence of one. When the neutral chlorine atom gains an electron it possesses an excess of *one* negative charge—and in the compound has a negative valence of one. This is paralleled by the financial status of two men, each with ten dollars in his pocket—and each with debts of ten dollars. They are financially neutral. However, if A gives B one of his dollar debts and B foolishly assumes the debt, A becomes worth $10 - 9 = 1$ dollar (a positive dollar), while poor B, now loaded with an extra liability, becomes worth $10 - 11 = -1$ dollar (a negative dollar). Here a dollar debt is an electron, and a dollar in pocket is a proton.

Neutral elements have no valence. It is only in compounds, after electrons have been given away or taken up, that they possess valence. An element such as a metal or hydrogen that has given away one electron has a positive valence of one; if it has given away two electrons, it has a positive valence of two. An element that has gained one electron has a negative valence of one; if it has gained two electrons, it has a negative valence of two.

In any compound the algebraic sum of the positive and negative ~~valences is zero.~~ Thus in H_2O the total positive valence of the two hydrogen atoms is two and the negative valence of the oxygen atom is also two.

By Abegg's old rule the mere numerical sum of the positive and negative valence possible for any element always equals eight.

Primary and Secondary Valence.—As Wyckoff well puts it, "the forces which cause atoms to combine in definite proportions to form molecules may, for convenience, be termed ***primary valence***

and the forces which unite these molecules into crystalline aggregates may be called ***secondary valence*** or residual valence. Secondary valence forces may serve to unite like molecules as well as unlike.

"The heat of formation of molecules due to secondary valence is, in general, very much smaller than the heat of formation of compounds and corresponds in magnitude with the heats of fusion and evaporation."

Metallic elements are (so far as known) monatomic in the gaseous state and consequently secondary valence forces hold them together in the solid state.

Oxidation and Reduction in Terms of Electrons.—Although the original conception of oxidation meant the addition of oxygen to an element or compound and reduction just the opposite, the loss of oxygen, we advanced later to a broader view.

Increase in valence of the central positive element in a compound came to be considered as oxidation and decrease in valence as reduction. For example, the process

$$2\,FeCl_2 + Cl_2 \longrightarrow 2\,FeCl_3$$

involving an increase in the valence of iron from two to three was recognized as oxidation of ferrous chloride to ferric chloride. The free chlorine bringing this about was called the oxidizing agent. Since an iron nail in a solution of ferric chloride removes one third of the combined chlorine the process of reduction of $FeCl_3$ may be represented as follows:

$$2\,FeCl_3 + Fe \longrightarrow 3\,FeCl_2.$$

Metals, then, may be considered as reducing agents in some instances. The free element iron above with zero valence became ferrous chloride with a valence of two. When metallic calcium burns in air it is oxidized: its valence is increased from zero to two by addition of oxygen.

$$2\,Ca + O_2 \longrightarrow 2\,CaO.$$

In terms of valence, oxidation may involve an increase in positive valence (or a decrease in negative valence). When calcium burns in oxygen it is true that the metal has its positive valence increased, is oxidized, but it is also true that the oxygen is reduced, for its valence is changed from zero to two (negative). Reduction is always the opposite of oxidation and always occurs simultaneously with oxidation. Two substances of opposite type react with each other with a definite numerical balance of changes in positive and negative valence. The present conception of oxidation and reduction follows.

Since a loss of electrons (negative changes) leaves an excess of positive charges on the previously neutral atom it is clear that the positive valence of that element has increased, it has been oxidized. In the reaction ($2\ FeCl_2 + Cl_2 \longrightarrow 2\ FeCl_3$) one iron atom in each molecule of ferrous chloride has lost one electron (to a neutral chlorine atom) and so has been oxidized. The positive valence of sulfur in SO_2 is four, therefore in the oxidation of this compound to SO_3 where the sulfur has a positive valence of six there must be a loss of two electrons (equivalent to increasing the positive charge by two). Free oxygen atoms take up these electrons, although slowly in the absence of a helpful catalyst.

$$2\ SO_2 + O_2 \longrightarrow 2\ SO_3.$$

Oxidation is the loss of electrons by the atom or substance oxidized. Reduction is the gain of electrons by any substance reduced. (There is a type of reaction in which a pair of electrons is shared by two atoms. Yet even in this instance it is possible that each electron is more closely held by one of the atoms than by the other.)

EXERCISES

6. Does this rule hold for Fe_2O_3 in which iron has a valence of three? When magnesium unites with chlorine, how are the electrons lost and gained? Look up magnesium chloride in the index and learn its correct formula.

7. Define valence. How is it measured?

8. In refreshing your memory as to the valence of an element, what is the advantage of looking up the correct formula of the chloride (index)?

9. In the laboratory how could you measure the equivalent weight of zinc (two methods)? Are these methods possible for copper?

10. What is the structure of an atom?

11. Define positive valence; negative valence.

12. How much zinc acting on any acid will be required to release as much hydrogen as would be obtained by the action of 1 Kg. of iron (90 per cent pure)

on steam? Compute this in one operation by the use of the equivalent weights of the metals.

13. If 26 g. of chromium displace 1 g. of hydrogen from hydrochloric acid what is the valence of chromium in this displacement (see Table of Atomic Weights)?

14. Assuming that chlorine is monovalent and that oxygen is divalent, state the valence of each of the metals in the following compounds: MgO, $AgCl$, $AlCl_3$, FeO, Fe_2O_3, SnO_2, Cr_2O_3, $NiCl_2$, $AuCl_3$.

15. Cobaltous oxide is CoO; cobaltic oxide is Co_2O_3. Write formulas for two types of cobalt compounds containing any of the following groups: Cl, NO_3, PO_4, SO_4.

CHAPTER VIII

WATER AND HYDROGEN PEROXIDE

Water

History.—Cavendish, not content with his pioneering study of the properties of hydrogen, added to his laurels by synthesizing water by burning hydrogen in air and in oxygen. Lavoisier decomposed water with red-hot iron and clearly interpreted Cavendish's experiments. In 1800 Nicholson and Carlisle decomposed water into its elements by electrolysis.

Occurrence.—Water is the most essential and most abundant compound. Three fourths of the earth's surface is covered with water, and in the form of vapor it is an indispensable part of the atmosphere. It makes up over two thirds of the human body. In fact there is truth as well as humor in the description of a man as "twelve pounds of ashes and eight buckets of water." Plant tissue contains from 50 to 75 per cent water. Celery is 94.5 per cent water, cabbage 91.5 per cent, eggs 73.2 per cent, and beef 60 per cent. Evidently moisture in the soil and in the air is necessary to plant life. Water evaporates from the oceans, rivers, and lakes, or, in other words, turns into the gaseous state. In this form it is carried over the land, and, when sufficiently cooled in the upper air, is precipitated as rain. Thanks to the sun's heat (aiding evaporation) and to the wind currents, this process is repeated indefinitely. A cubic mile of air can hold so much moisture on a very hot day that if suddenly cooled to freezing it would precipitate 140,000 tons of water.

One inch of rain on the United States corn belt at the critical time in the growing season is worth $400,000,000. This inch on a single acre weighs 113 tons.

Physical Properties.—Pure water is colorless in thin layers, but in thick layers is blue. However, we do not find absolutely pure water in nature. Fine suspended material of a yellowish tint, or light reflected from the yellow sand of a river bottom, must modify the natural blue to green. No wonder the ocean and deep lakes seem blue or green. Pure water is odorless, yet from some springs offensive hydrogen sulfide water flows. Pure water is also tasteless; in other words it tastes "flat." The pleasant taste of good drinking water is due to dissolved air and carbon dioxide. This explains why boiled water is so unpalatable.

One cubic centimeter of water at 4° C. weighs one gram, so by definition its ***density*** is one. It expands on warming above or cooling below this point. When formed under enormous pressure denser varieties of ice appear. A fortunate thing it is that common ice is lighter than water. Otherwise as fast as the water on the surface of a northern river or lake froze it would sink and the lake would soon be solid to the bottom. In deep waters the summer sun would accomplish little. Fish would become extinct in a single cold winter. The ***specific heat*** of water is 1, which means that it requires one calorie of heat to raise one gram of water one degree. This is greater than the specific heat of almost every other substance. It is for this we prize a hot-water bottle — at times—and enjoy a hot-water heating system. Since the specific heat of many common rocks is only one fifth that of water, it is evident that great bodies of water heat up slowly and cool off slowly in comparison with land, thus moderating the climatic changes.

Under 760 mm. pressure liquid water becomes solid ice at 0° C. and gaseous steam at 100° C. In melting one gram of ice at 0° C. into water at 0° C. 79 calories of heat must be absorbed. Conversely, on freezing one gram of water releases 79 calories. This is called the ***heat of fusion of ice.***

One gram of water at 100° C. requires 540 calories of heat to change into steam at 100° C. On condensing this steam into water, the same 540 calories of heat—the ***heat of vaporization***—are released. No wonder steam is so efficient in heating houses. It takes a great deal of heat to "raise steam" in the boiler, but we get it back in the radiators, which are merely convenient steam condensers.

Composition of Water by Weight. (Morley's Work).—The weight proportion of hydrogen and oxygen in water were determined by Dumas by reduction of heated cupric oxide with hydrogen (page 12). However, for marvellous accuracy the classic determination by E. W. Morley of Western Reserve University has never been surpassed. Morley used the glass apparatus represented in Figure 40 except that he sealed the entrance tubes at *A* and *B* instead of using stopcocks. Carefully dried pure hydrogen from weighed globes entered at *A* into the evacuated and weighed apparatus while pure dry oxygen from another weighed globe entered at *B*. After passing through guard layers of the powerful dryer, phosphorus pentoxide, the two gases met at *D* where a stream of electric sparks caused a continuous formation of water. This steam was condensed and finally frozen in the tube *C* by immersing the lower end in a freezing mixture. At the end of the experiment the two globes from which the gases were drawn were weighed in order to indicate the weight of oxygen and hydrogen used. However, the residual gases in the tube had to be drawn off at *A* and *B* and analyzed. Thus the weights of hydrogen and oxygen originally drawn into *C* were corrected to show the weights actually reacting. A final weighing of the reaction apparatus showed an increase in weight due to the water formed. Of course the residual gases withdrawn from *C* carried some moisture with them, but this was retained by the phosphorus pentoxide dryer in the guard tubes.

As an average of twelve experiments Morley found the ratio of hydrogen to oxygen by weight in water to be 1 part of hydrogen to 7.94 parts of oxygen. At this ratio how much hydrogen must unite with exactly 8 g. of oxygen? Morley found the volume ratio to be 2.00269 volumes of hydrogen to 1 volume of oxygen.

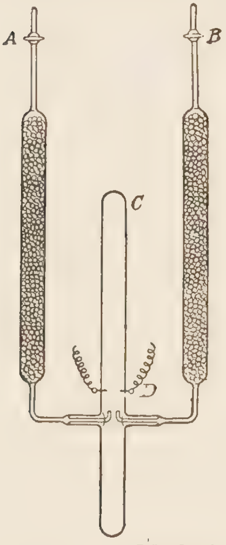


FIG. 40.—Morley's apparatus.

Chemical Properties.—When heated to 1000° water begins to *dissociate* or break down into hydrogen and oxygen. At 2000° 1.8 per cent is dissociated. Of course the two elements are recombining all the time, and at each new temperature a new equilibrium is found.

At 2000°

$$\underset{1.8\%}{H_2 + O} \rightleftarrows \underset{98.2\%}{H_2O.}$$

EXERCISE 1.—Can any other form of energy than heat be used to decompose water?

The following may be as much a physical as chemical property; but however that may be, it is of fundamental importance. Water is the greatest catalyst we have. Ordinarily we merely say that it aids reaction. Two substances very intimately mixed (dissolved) in water are in better contact than is possible without the water. There is also another helpful effect to be discussed later (see Ionization). Many reactions, perhaps nearly all, require at least a minute trace of moisture. A mixture of absolutely dry oxygen and hydrogen cannot be exploded.

Water reacts with some elements, such as chlorine and sodium:

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl,$$
$$2\ Na + 2\ H_2O \longrightarrow 2\ NaOH + H_2.$$

With ammonia it forms the soluble base, ammonium hydroxide:

$$NH_3 + H_2O \rightleftharpoons NH_4OH.$$

Exercise 2.—What metals react with cold water? What metals react with steam only when very hot? Can carbon be made to react with water?

Hydrates.—Certain substances crystallize from their water solutions on slow evaporation of the liquid, carrying definite amounts of the water with them. This ***water of crystallization,*** as it is sometimes called, is not held in a wet sponge fashion, for no amount of pressure will squeeze it out. Moreover a sponge can hold any amount of water, within wide limits. Not so these ***hydrates*** which we are discussing. Hydrates must be definite chemical compounds because atomic weights are essential in expressing their composition. Some substances, it is true, can crystallize with two or three definite amounts of water, but the shape of the crystals, solubility, and some other properties are then different. These hydrates feel dry to the touch but easily lose their combined water on heating. On adding the heated product to water the same solution is obtained as if the crystals had been used. For example, blue vitriol is a hydrate with five molecules of water of crystallization, $CuSO_4 \cdot 5\ H_2O$. When heated above 200° all the water is lost and a white powder is obtained, $CuSO_4$. Under favorable conditions this can be obtained in crystals of a different shape. But add either $CuSO_4 \cdot 5\ H_2O$ or $CuSO_4$ to water and the same blue solution results in either case. On careful evaporation of the two solutions both produce blue crystals of $CuSO_4 \cdot 5\ H_2O$:

$$CuSO_4 + 5\ H_2O \longrightarrow CuSO_4 \cdot 5\ H_2O.$$

Dehydrated copper sulfate gives off 18,500 calories of heat when a gram-moleculer weight, or mole, of it unites again with as much water as it held in its original form of $CuSO_4 \cdot 5\ H_2O$.

Such hydroxides as we have known so far ($NaOH$, $Ca(OH)_2$, and KOH) can also be formed by the union of water with the proper metallic oxide.

$$CaO + H_2O \longrightarrow Ca(OH)_2,$$
$$Na_2O + H_2O \longrightarrow 2\ NaOH.$$

Hydrates, however, are well-crystallized compounds formed by the union of water with compounds, such as $CuSO_4$, or even with an element, such as chlorine (p. 162). Some hydroxides, like hydrates, lose water readily on heating. Silver hydroxide loses water as fast as it is formed at ordinary temperatures, so that we secure only silver oxide. In fact the oxide may be drowned with water, but it refuses to hold any of it. In hydrates the water molecules retain their identity while in hydroxides the water lost on heating comes from the –OH groups.

We noted in a previous chapter that a few drops of water let into the vacuum at the top of a barometer forces the mercury down several millimeters, an increasing distance with rise in temperature. This pressure, called ***vapor tension*** when at its maximum for a given pressure, is merely the partial pressure of water vapor. Now if instead of drops of water a crystal of sodium sulfate, $Na_2SO_4 \cdot 10\ H_2O$, is introduced into the barometer tube, the mercury falls almost as much as for water itself and the clear crystal crumbles to a white powder. Some other hydrates depress the mercury less. The depression in millimeters is a measure of the tendency of the water to evaporate. Place a clean crystal of $Na_2SO_4 \cdot 10\ H_2O$ in the open air and it soon crumbles to a white powder weighing far less. Evidently the outward pressure (aqueous tension) of the water in the crystal is greater than the opposing pressure of water vapor in the air. Such loss of water from hydrates at room temperatures is called ***efflorescence.*** Washing soda, $Na_2CO_3 \cdot 10\ H_2O$, acts in similar manner. Other hydrates lose little or none of their water in air, blue vitriol, for example. This means that the aqueous tension of $CuSO_4 \cdot 5\ H_2O$ cannot more than slightly exceed that of ordinary air. It might be less. But in absolutely dry air blue vitriol loses water.

The Boiling Point of Water.—Water in an open vessel boils when its aqueous tension equals the pressure of the air, as stated on page 60. Then with violent bubbling and breaking of its surface it changes into steam. The boiling point of water is 100°

when the air pressure is 760 mm., but on top of Mt. Blanc water boils at 84.4° because the pressure averages 424 mm. So we understand why campers on a high plateau might boil potatoes to the limit of patience without any nutritious result. It is temperature that cooks potatoes and other foods, not the mere violent ebullition we call boiling. If we evacuate the air from a bell jar containing a beaker of cold water, the water boils violently because its aqueous tension at last equals the decreased pressure of the air. Pressure cookers are great aids in the speedy and economical cooking of tough meats. With a lid clamped on tightly the steam soon raises the pressure so that the boiling point of the liquid present is raised. In other words the meat can get hotter than in an open vessel under a pressure of one atmosphere.

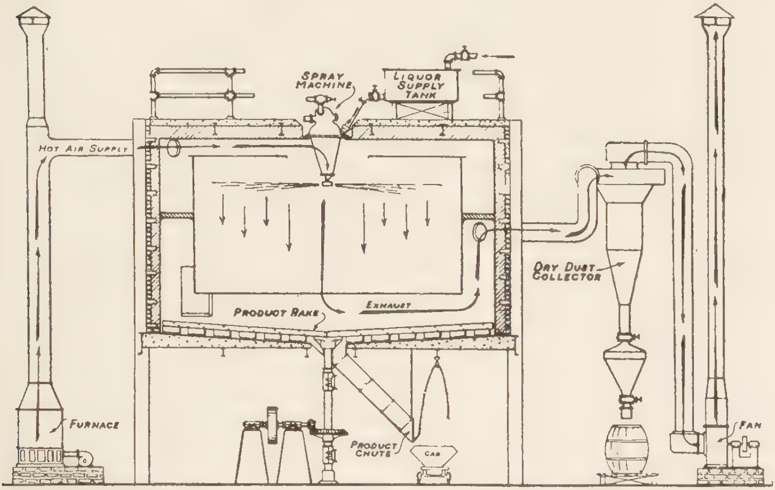


FIG. 41.—Almost instantaneous drying of wet sludges by spraying into a hot-gas chamber. The solid product usually consists of little spheres.

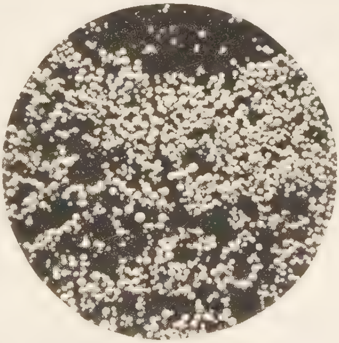


FIG. 42.—Spherulites from spray drying of monocalcium phosphate.

EXERCISE 3.—How does a hydrate differ from a solution or from a hydroxide?

Exercise 4.—If water vapor above the mercury in a barometer tube were heated to 100°, how high a column of mercury would still remain below it? It is understood that sufficient excess of water is present to keep the vapor saturated.

Natural Waters.—The average annual rainfall of the United States is 27.6 inches falling an average distance of 7920 feet. It would require a three-horse-power engine working on every acre to raise this quantity of water to such a height. Yet the sun's heat through evaporation and air currents accomplishes this great task. Water is the most nearly universal solvent we have. Most substances are dissolved by it to at least a minute extent.

Is it any wonder then that rain water dissolves rock material and gradually carries it to the sea? Freezing, with its expansion of water in crevices, disintegrates rock and is aided by the force of waves and currents. But for such wonderful provisions of nature our soil would be a barren rock.

Among the rocks most easily dissolved are the carbonates of calcium and magnesium known as limestone and dolomite. Water containing a little carbon dioxide from the air is particularly effective. For this reason the water in limestone regions is very "hard." This hardness is not dangerous to health, in fact some think it healthful, but it causes great waste of soap in washing and a great waste of heat in boilers by causing the formation of boiler scale. We often try to remove much of this hardness by adding chemicals to soften the water. The important subject of water softening will be taken up in detail when we study calcium.

It is not merely rock material that is contained in the water of wells, springs, lakes, and streams. Rain water washing the surface of the ground dissolves dead plant material and animal refuse, sometimes to such an extent as to take on a brownish color and slight odor and taste. But the worst feature of this "carry-all" nature of water is its ability to pick up bacteria that cause disease, typhoid, for example.

The experience of Plymouth, Pa., points a warning. One winter a typhoid patient was nursed in a house located on the watershed draining into the town's reservoir. When the snow melted some months later the house refuse was washed into a brook leading directly into the reservoir. At that time this water was untreated and the resulting epidemic of typhoid fever caused

114 deaths in a city of only 8000 people. Sewage should never be allowed to contaminate drinking water.

Purification of Water.—Dangerous bacteria in drinking water may be killed by small amounts of chlorine. This gas is soluble in water, so mixing is simple. Many great cities treat their water supply in this way. If too much chlorine is added, a slightly unpleasant taste is noticed, but this excess is not necessary. The average amount of chlorine used in water supplies is about 2.5 pounds per million gallons and the excess above the amount used up in reaction should never exceed 0.5 pounds per million gallons. Bleaching powder, a chlorine product, is about as effective as chlorine.

The universal method of treatment is sand filtration (Fig. 43). Nearly all city filters are built up of a layer of gravel covered by coarse sand, and then a layer of finer sand, several feet deep in all. A good sand filter not only catches mud but catches practically all the bacteria. The best American practice is to let the sediment in the "raw" water settle out in large basins before filtering. This saves the filter from too great a load of mud. The average city of 100,000 uses 10,000,000 gallons daily.

Many small towns and even larger cities (Columbus, Ohio, is a notable example) soften their water supply by adding lime and soda. The further addition of aluminum sulfate (wrongly called "alum") forms a precipitate which drags down nearly all the bacteria on settling, so both softening and purifying are accomplished in one operation.

Pure drinking water may be obtained by distillation (Fig. 23), but the distillate has a "flat" taste, due to the lack of air and carbon dioxide.

In the Spanish-American War, lack of sanitary precautions led to a greater loss of life in the army than that due to fighting. A great part of this loss was due to the entrance of typhoid bacteria into the camp water. In the World War our

FIG. 43.—Section of a municipal filter bed showing fine sand resting on coarse sand and gravel, from which the water is drained into pipes.

army benefited greatly by extreme care in the supply of pure drinking water. Whipple says that records kept in twelve of our greatest states show that the deaths from typhoid in 1880 were 55 per 100,000 population and in 1910 only 19 per 100,000. In 1927 the typhoid death rate for 32,000,000 urban population fell to 1.96 per 100,000. This improvement was largely due to purification of drinking water and to pasteurization of milk. The old-fashioned idea that clear, sparkling, palatable water must be pure has been exploded. It may be as dangerous as a cup of poison if it carries the germs of typhoid.

Fig. 44.—When Witigis, King of the Goths brought his hordes to the siege of Rome in the year 537, he dealt a deadly blow at the city by striking at the aqueducts which furnished Rome with water.

Chicago once dumped its sewage into Lake Michigan and drew its city water from the same lake. Finally the Chicago River was deepened and its current reversed into the Mississippi system, thus making the river a sewage canal. The death rate from typhoid quickly fell from 170 per 100,000 to 16 per 100,000. Many cities now treat their sewage so that a safer effluent is discharged into the rivers.

Nature's methods of purifying river water are interesting. The dissolved organic material is decomposed by bacteria. Sewage is used up, to a great extent, by snails, beetles, mussels, worms, insect larvæ and other organisms.

HYDROGEN PEROXIDE

Hydrogen peroxide resembles ozone in its "safe and sane" oxidizing action on delicate materials. These two substances are often studied together. We buy hydrogen peroxide as a 3 per cent solution in water.

Preparation.—A convenient laboratory method of preparation is to drop sodium peroxide slowly into ice water:

$$Na_2O_2 + 2\,H_2O \rightleftarrows H_2O_2 + 2\,NaOH.$$

If too much sodium peroxide is added too rapidly, the heat of reaction decomposes the product desired into water and oxygen. The following reactions may also be used in preparation of this compound:

$$\begin{array}{lr} (1) & Na_2O_2 + H_2SO_4 \longrightarrow H_2O_2 + Na_2SO_4, \\ (2) & BaO_2 + H_2SO_4 \longrightarrow H_2O_2 + BaSO_4, \\ (3) & BaO_2 + H_2CO_3 \longrightarrow H_2O_2 + BaCO_3, \\ (4) & 3\,BaO_2 + 2\,H_3PO_4 \longrightarrow 3\,H_2O_2 + Ba_3(PO_4)_2, \\ (5) & BaO_2 + 2\,HCl \longrightarrow H_2O_2 + BaCl_2. \end{array}$$

Reaction (2) is the one favored commercially. The barium sulfate, being insoluble, is filtered off. In fact reactions (3) and (4) are good and (5) is poor because we prefer to filter off an insoluble barium salt, leaving in the filtrate only hydrogen peroxide and water free from any poisonous barium salt. The barium chloride of (5) is soluble, while the carbonate, phosphate, and sulfate of barium are insoluble. Sodium sulfate does no harm.

Pure hydrogen peroxide is difficult to make and almost impossible to keep. If an attempt is made to boil off the water from the usual solution, the peroxide decomposes. But by boiling under diminished pressure, at 68 mm., water is removed at 85° and a syrup obtained. It explodes on very slight provocation such as contact with manganese dioxide.

Properties.—Anhydrous hydrogen peroxide is a colorless, syrupy liquid with a slight odor resembling that of nitric acid and with an astringent, bitter taste. At 0° it is a liquid with a density of 1.4584 while at $-2°$ it freezes. It mixes with water in all proportions and is comparatively stable in such solutions. Light decomposes it, so brown bottles are the best containers. The trace of alkali from the glass decomposes it but a very little acid can counteract this tendency by reacting with the alkali. Usually a trace of acetanilide is used to check decomposition:

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2.$$

The above reaction is caused by bases, finely divided gold, platinum, manganese dioxide and many other substances which are themselves unchanged, therefore acting as catalysts. Many neutral salts dissolve in pure hydrogen peroxide without causing any decomposition.

The oxidizing power of hydrogen peroxide is its most valuable property. However, the action is not vigorous, and a harmless by-product, water, is formed. Hence its popularity as a gargle and for other medicinal uses. Its ability to kill bacteria, although real, has been greatly overestimated by the public. On pus and blood it reacts with effervescent release of oxygen. This gassing makes it ideal for the gentle loosening of dried bloody bandages. Its gentle oxidizing action makes it invaluable for bleaching silk, feathers, hair, ivory, and various delicate materials. A darkened oil painting may be lightened by cautious use of hydrogen peroxide. Since the darkening was partly due to the formation of lead sulfide from the lead paint, the remedy is oxidation of this dark compound to white lead sulfate:

$$PbS + 4\,H_2O_2 \longrightarrow PbSO_4 + 4\,H_2O.$$

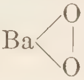
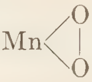
Tests.—Like ozone, hydrogen peroxide releases free iodine from hydrogen iodide. In the presence of starch this iodine develops a blue color. A filter paper dipped in a solution of potassium iodide and starch paste (slightly acidified to release the acid) serves as a rough test, but as the oxygen of the air also releases free iodine (though slowly) from hydrogen iodide, the test is good only if a blue color forms almost instantly:

$$H_2O_2 + 2\,HI \rightleftharpoons I_2 + 2\,H_2O.$$

Traces of hydrogen peroxide may be detected by the addition of dilute sulfuric acid and *very* dilute potassium dichromate ($K_2Cr_2O_7$). A blue color develops but quickly fades unless a layer of ether has been shaken quickly with the solution. The blue perchromic acid formed is more soluble in the ether layer and is stable there. With a solution of titanium sulfate, hydrogen peroxide produces orange-yellow pertitanic acid. Very faint colored potassium permanganate loses its pink color if hydrogen peroxide is added, especially if catalyzed by a little magnesium sulfate. This is confirmatory evidence in a test, although some other substances do the same thing. This last reaction of mutual reduction is the basis of an important quantitative method for determining hydrogen peroxide:

$$2\,KMnO_4 + 5\,H_2O_2 + 3\,H_2SO_4 \longrightarrow K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,O_2.$$

Exercise 5.—If a solution of potassium permanganate is just decolorized by 150 cc. of hydrogen peroxide (3 per cent by weight), how many grams of the permanganate must have been used? How many grams of oxygen escaped? Assume that the density of the hydrogen peroxide solution is practically one.

Peroxides.—The structural formula of water is H—O—H and of hydrogen peroxide H—O—O—H. Evidently sodium peroxide, Na_2O_2, is a salt derived from the feeble acid H_2O_2 by replacing the hydrogen with sodium. (This is not done directly, however.) Na—O—O—Na is the structural formula for this oxide. When BaO_2 is acidified H—O—O—H is formed, so  must represent the structure. But MnO_2 when acidified does not yield H_2O_2. Hence its structure must be O=Mn=O and not . Peroxides yield hydrogen peroxide when acidified and dioxides do not. MnO_2 and PbO_2 should be called dioxides. In the true peroxide linking, two oxygen atoms are directly attached to each other.

EXERCISES

6. If a crystal of a given hydrate does not lose water in the open air at 20°, how could you force it to effloresce?

7. Would all hydrates effloresce in a vacuum?

8. Lead dioxide, PbO_2, does not yield H_2O_2 when treated with an acid (H_2SO_4, for example). What, therefore, must be the structural formula of this oxide of lead?

9. What is meant by the heat of fusion of ice? By the heat of vaporization of water? By efflorescence?

10. What influence has water on chemical reactions?

11. Why are hydrates definite chemical compounds?

12. How much chlorine per million gallons is used in water purification?

✓ 13. Morley found the composition of water by determining the weights of hydrogen and oxygen that combine with each other to form water. The results of four trials were as follows:

Hydrogen Used	Oxygen Used	Hydrogen Used	Oxygen Used
3.2645 g.	25.9176 g.	3.8193 g.	30.3210 g.
3.2559 g.	25.8531 g.	3.8450 g.	30.5294 g.

In each case calculate the ratio in which hydrogen and oxygen combine.

✓ 14. Glauber's salt is a hydrate of sodium sulfate. If 12 g. of Glauber's salt, when heated loses 6.72 g. of water, what is the formula of the hydrate?

√ 15. How many grams of water could be heated from 0° to 100° by the heat required to melt 1 Kg. of ice at 0°?

√ 16. If 100 cc. of hydrogen and 74 cc. of oxygen are exploded in a closed tube, which gas remains? How much?

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CHAPTER IX

CARBON AND ITS OXIDES

Carbon

Fully 250,000 compounds of carbon are known (though not by any one man). All other compounds together make up only a small fraction of this impressive number, perhaps 25,000. Carbon chemistry was named Organic Chemistry because it was once thought that only organized living matter could produce carbon compounds. In other words, only plants and animals qualified as synthetic carbon chemists. But since 1827 an infinite number of these compounds have been made in the laboratory.

The importance of carbon and its compounds is evident as we learn that they make up our fuels, whether coal, wood, oil, or gas; our lubricants; our foods; our clothing; and that they make possible the change from iron to steel. Drugs, dyes, explosives, pencils, printer's ink—these and a host of other necessities are based upon carbon and its compounds.

This element is tetravalent as shown by the compounds CH_4, CCl_4, and CO_2 and is a non-metal as indicated by its hydroxide (H_2CO_3), a weak acid. It resembles silicon, tin, and lead of the same group in some respects, although not metallic like tin and lead.

The element occurs in nature in two crystalline forms, the diamond and graphite, and is readily prepared from its compounds in such amorphous forms as coke, lampblack, charcoal, boneblack and gasblack.

The Diamond.—The diamond is a pure form of carbon crystallizing in the regular system. It is the hardest substance known and hence scratches all other substances. Faulty specimens are used for the cutting edge of rock drills and in the form of dust to polish good diamonds. Its density, 3.5, is greater than that of graphite and the other forms.

About $60,000,000 of diamonds were mined in 1927, most of them in South Africa, and at that the output was restricted in order to keep up the price. The largest diamond ever found, the

Cullinan, weighed 3024 carats. Since the carat (metric) now equals exactly 0.2 g. this means a crystal of 605 g., or 1.37 pounds. The magnificent Regent diamond, to be seen at the Louvre weighs 136 carats.

The cost gives the diamond much of its charm, but it has a real beauty when skillfully cut. This is due largely to its high index of refraction. Rays of light are reflected from the interior surfaces of the facets several times before emerging, hence the flashing play of light.

In 1894 Moissan prepared synthetic diamonds, but unfortunately the largest was only half a millimeter in diameter. He dissolved pure carbon (from sugar) in molten iron and suddenly chilled the crucible by dropping it in water or in molten lead. A solid shell instantly formed, but the interior solidified more slowly. As iron expands on solidifying, enormous pressure must have been developed. As the carbon, soluble only in very hot iron, came out of solution it crystallized in diamond form. Pressure and high temperature were necessary—the same conditions as those found in the depths of the earth. The iron was dissolved away from the diamonds by acid.

Graphite.—Graphite is a crystalline form of carbon differing noticeably from diamond. It is black, soft, and made up of six-sided leaflets which slide easily over one another. It is lighter than the diamond, having a density of only 2.25. Chemically it is quite inactive, yet it is possible to burn it at very high temperatures.

The most important deposits are in Ceylon, and Madagascar.

When any form of carbon is heated in the electric furnace it turns into graphite; in fact carbon volatilizes at 3500° without melting and on cooling condenses as graphite. This is the basis of Acheson's method of making artificial graphite at Niagara Falls. A bank of anthracite coal is heaped up and large electrodes inserted at the ends. On passage of a heavy current (40,000 amperes and 200 volts) the heat generated is enough to bring about the desired change. This change is greatly helped by sand or iron oxide which probably form intermediate compounds that decompose, yielding graphite. It was found that the ash of coal furnishes enough of these catalysts. The Acheson process produces over 13,000,000 pounds per year, yet the country uses ten times that amount of graphite, natural and artificial.

Graphite is the essential constituent of lead pencils. Mixed with clay it is molded and baked, and then glued in the groove between two halves of the wooden rod. The harder pencils contain more clay. As a lubricant it is useful where wooden parts rub or where high temperatures or pressures are attained. Acheson prepared a valuable suspension of graphite in water called "aquadag" by the action of tannin as a disintegrating agent. The water merely helps the real lubricant, graphite, to reach all parts of the bearing surface. The same is true of the suspension of graphite in oil called "oil-dag." Acheson remembered the Biblical story of the Israelites who were compelled by the cruel Egyptians to make "bricks without straw." ~~He re~~asoned that the straw did not act as a mechanical binder but had a chemical action on the clay. This he proved by extracting tannin from straw and then adding the extract to clay. It disintegrated the clay into marvelously fine particles which held together better in making sun-dried bricks. The action of tannin on graphite to form minute particles for better lubrication is a parallel to this.

Graphite is much used as a stove polish to prevent rusting, and in black paints for the same reason, although there is some dispute as to its merits. Since it stands high temperatures, crucibles are made of graphite and clay mixed in the right proportions. Unlike the diamond, graphite conducts electricity well, so a film brushed on any surface, whether wood or wax, makes it possible to suspend the coated object as cathode in a solution of copper sulfate and to electroplate a layer of copper on it. This has wide application. In the electrolytic decomposition of sodium chloride, the chlorine released at the anode attacks nearly all substances, so graphite electrodes are preferred because they are not affected.

Amorphous Carbon.—There are several forms of amorphous carbon, such as coke, charcoal, and soot, but none of these occur in nature. Bituminous coal probably contains little if any free carbon because there are certain liquids which dissolve practically all of a given quantity of coal. At ordinary temperatures there is no solvent for free carbon. These amorphous forms are made by decomposition of carbon compounds as by dry distillation without access of air. The density, hardness, and electrical conductivity of all forms of amorphous carbon are increased by high temperature treatment.

Coke.—When bituminous coal is heated in retorts without access of air, many volatile products escape. These include ammonia, illuminating gas, and coal tar, from the last of which benzene, toluene, phenol (carbolic acid), creosote, naphthalene, and many derivatives of great value are secured. Coke is left behind in the retort. It is used in making pig iron from iron ore, in melting metals for foundries, as a domestic fuel, and in the manufacture of some carbon compounds.

About 90 per cent of our total coke production of 60,000,000 tons are produced in by-product ovens.

Coke burns with almost no flame and no smoke. It is impure carbon since the ash of the coal is still in the coke.

Coal.—The forests of previous ages were buried under deep layers of earth and so subjected to great heat and pressure. This caused a loss of much volatile material and left coal. Peat is a product formed from accumulations of swamp growth. It burns when dry but has a low fuel value. Enormous peat bogs are found in Russia, Ireland, Canada, and the United States. Lignite, or brown coal, represents an early stage in nature's coal making, hence lignite has only moderate fuel value. Enormous deposits are found in South Dakota and other Western states. Bituminous or "soft" coal represents a more advanced stage of coal making in the earth. It yields much volatile matter on distilling and burns with a smoky flame. The fuel value of the best soft coal is high. Anthracite or "hard" coal is almost the final product in coal making. It is older, nearly all volatile matter has been driven off in the depths of the earth, and consequently the anthracite is hard, yields but little volatile matter on destructive distillation, and burns with no smoke and but little flame. Its fuel value is high. The greatest anthracite deposit in the world is found in eastern Pennsylvania.

The United States is particularly fortunate in its wealth of coal. The world produces about 1,300,000,000 tons annually and of this over 45 per cent is mined in this country. England and Germany follow the United States in coal production. Such deposits act as an industrial and military weapon of the utmost mon value.

Charcoal.—Wood charcoal was once used in metallurgy in place of the coke of modern times and it is still in some demand. Cheap black gunpowder requires it. Just as coke is the non-volatile product of coal distillation, so is charcoal the residue remaining when wood is destructively distilled. By modern methods all the volatile products are condensed and used in many important industries. Among these products are wood alcohol, acetone, and acetic acid.

Bone charcoal is made by distillation of bones after all the fat has been removed and the bones steamed for glue and gelatine products. This form of carbon contains much calcium phosphate, which can be removed by treatment with acid. This boneblack is in great demand by sugar refiners. Solutions of crude cane sugar having a slight yellow tint are filtered through a large cylinder containing tons of boneblack. This material, made up of very fine particles, exposes enormous surface to the syrup and holds (adsorbs) the coloring matter of the sugar. The filtrate runs through clear and yields the purest granulated white sugar on evaporation. The adsorptive power of charcoal for various liquids and gases has made it useful in a number of purification processes.

During the Great War the adsorption of poison gases by cocoanut charcoal in the gas mask was the main defense against gas attack. In fact an army without such an adsorbent material could now be demoralized and defeated with poison gases.

Carbon Black.—When a smoky gas flame is chilled the incandescent carbon of the yellow flame deposits as a form of soot called ***carbon black.*** An inferior carbon called ***lampblack*** is prepared by chilling the smoky flame from tars and oils.

Carbon black is essential to the manufacture of printer's ink and some rubber goods. It gives auto tires (about 2 lbs. per tire) great toughness, resiliency, and wearing qualities. These two blacks are also used in the manufacture of paints, stove polish, phonograph records, carbon paper, crayons, black leather, and other articles. Over 175 billion cubic feet of natural gas are burned annually in the United States making about 250,000,000 pounds of carbon black. Common black smoke is not pure carbon by any means. Nor is it an asset to a city. A year's soot fall on a square mile of London weighs 260 tons.

Physical Properties of Carbon.—Carbon in any form is an odorless and tasteless solid, either colorless, as in the diamond, or black, as in graphite. The different forms are not of the same density or hardness or electrical conductivity. Exposure of the amorphous forms to intense heat converts them into the graphite modification. Carbon is insoluble in ordinary solvents but is dissolved to a very limited extent by molten iron and a few other metals. Iron takes up 1 or 2 per cent of its weight of carbon, which on cooling crystallizes out as graphite. To be exact, only part of it separates, for some carbon reacts with iron to form iron carbide.

Chemical Properties.—Carbon is inactive except when hot. At higher temperatures it unites readily with oxygen to form carbon monoxide and carbon dioxide. It is our most important commercial reducing agent because when hot it removes oxygen from metallic oxides. This is one of the reactions taking place in the blast furnace:

$$Fe_2O_3 + 3\,C \longrightarrow 2\,Fe + 3\,CO.$$

With relatively little coke the dioxide escapes, but with an excess of coke the carbon monoxide predominates.

Carbon unites with hydrogen to a very limited extent in the electric arc to form acetylene, C_2H_2, and, by the catalytic aid of nickel powder at 250°, to form methane (CH_4).

Exercise 1.—This latter reaction is reversible and exothermic. If the materials were heated to 800°, what would the principle of Le Chatelier lead you to expect? Pressure would be lessened
Reaction would go both ways.

A carbide is a compound of carbon with one other element, usually. A carbide of iron is found in steel and has the greatest influence on the properties of the steel. Calcium carbide, CaC_2, which reacts with water to form acetylene, is the product of electric furnace heating of lime and coke. A carbide of silicon called carborundum, SiC, is the most useful abrasive known. Hot carbon also unites with sulfur to form carbon disulfide, CS_2.

Exercise 2.—What mention of calcium carbide is made in the chapter on nitrogen? unites with N to form calcium cyanamide

Oxides of Carbon

Carbon Dioxide, CO_2.—Carbon dioxide occurs in the air to the extent of 3 or 4 parts in 10,000 and issues from the earth in a few places. Some spring waters contain it in solution under pressure. As the water reaches the surface of the earth and the pressure is released the gas escapes with effervescence just as it does in soda water. Its occurrence in the air is due to combustion, the respiration of animals, decay, and fermentation. In a long life a man may exhale 20 tons of carbon dioxide. Joseph Black (1757) first recognized carbon dioxide as a distinct substance. He observed its formation by at least three reactions.

Preparation.—1. The simplest method of preparing carbon dioxide is by direct union of carbon and oxygen. The carbon must be burned with an excess of oxygen or part of the dioxide may be reduced to carbon monoxide by the hot carbon:

$$C + O_2 \longrightarrow CO_2,$$
$$CO_2 + C \longrightarrow 2\,CO.$$

But it is not necessary to burn pure carbon. Any carbon compounds, such as coal, wood, paper, and oils may be burned with formation of the dioxide. Any other elements present would probably burn to their oxides.

Exercise 3.—Balance the equations:

$$\text{Hot } CH_4 + O_2 \longrightarrow ?\ H_2O + CO$$
$$\text{Hot } C_2H_5OH + 2O_2 \longrightarrow ?\ 2CO_2 + 3H_2O$$

The first represents the burning of natural gas and the second the burning of alcohol.

2. High heating of some carbonates (but not of the carbonates of sodium and potassium) yields carbon dioxide. Potassium carbonate at 800° has a vapor pressure of less than 1 mm. Calcium carbonate is far more easily decomposed, magnesium carbonate more readily still. The manufacture of quicklime from limestone in the limekiln depends upon this reaction. In a closed tube this reaction is reversible, but not where the gas is removed:

$$CaCO_3 \longrightarrow CaO + CO_2.$$

3. The laboratory method is the treatment of carbonates, such as limestone or marble, with a dilute acid:

$$CaCO_3 + 2\,HCl \longrightarrow CaCl_2 + H_2CO_3,$$
$$H_2CO_3 \longrightarrow H_2O + CO_2.$$

The carbonic acid first formed is very unstable, and decomposes with escape of carbon dioxide.

4. The fermentation of sugar solutions to form alcohol yields carbon dioxide as one product.

Physical Properties.—Carbon dioxide is a colorless, odorless gas, one half heavier than air. At 15° water dissolves its own volume of the gas. The soda water of fountains contains much more in solution under about 10 atmospheres pressure. The solution has a slightly sharp, pungent taste. The gas is sold commercially in thick steel cylinders under 60 atmospheres pressure. Most of it is liquid. The liquid, allowed to es-

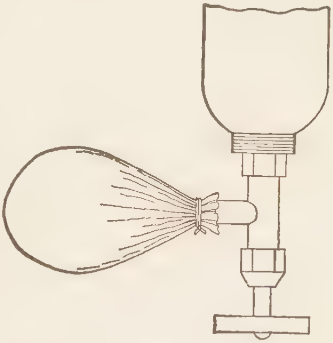


Fig. 45.—Making carbon dioxide snow.

cape from the inverted cylinder (Fig. 45), vaporizes so rapidly that it is quickly cooled to $-79°$, at which temperature it freezes to a snowlike solid. This may be caught in a cloth bag. Such carbon dioxide snow is now sold commercially in compressed blocks.

Some very spectacular experiments may be performed with this snow. Rapid evaporation of a solution of carbon dioxide snow in ether yields a temperature of $-110°$, making it a simple matter, by use of this mixture, to freeze mercury ($-40°$). If the mercury is placed in a small pasteboard box and a stick of wood held in it, a hammer is secured with a head of solid mercury. The pasteboard box is readily torn off and nails may be driven into a board with the hammer. A thin piece of beefsteak is "cooked" white and is so brittle it may be broken in pieces. A rubber ball thus chilled breaks to pieces when thrown against a brick wall. A frozen flower is extremely brittle and a frozen rubber tube may be snapped in two like a clay pipestem.

The critical temperature of carbon dioxide is 31.33°. At 20° its vapor pressure is 59 atmospheres.

Chemical Properties.—Carbon dioxide is so stable that its dissociation ($2\,CO_2 \rightleftarrows 2\,CO + O_2$) is only 1.8 per cent at 2000°. For this reason it does not support combustion except for very active elements. Magnesium burns in the dioxide, leaving black carbon. Carbon above 1000° (almost white heat) reduces carbon dioxide to the monoxide:

$$CO_2 + C \longrightarrow 2\,CO.$$

In a furnace full of a deep bed of brightly glowing coals the carbon dioxide formed at the bottom of the layer is probably reduced to the monoxide by the upper layers of incandescent coal. The monoxide then burns at the surface with a blue flame.

With metallic oxides carbon dioxide unites to form carbonates:

$$CaO + CO_2 \rightleftarrows CaCO_3.$$

Quicklime exposed to the air not only takes up moisture but reverts, as indicated by the equation, to calcium carbonate. It is then "air slaked." Ques

Carbonic Acid, H_2CO_3.—Since a water solution of carbon dioxide is weakly acid, there must be a reaction between water and carbon dioxide to form an acid, carbonic acid. On boiling, all the carbon dioxide is removed, so the reaction is evidently reversible:

$$H_2O + CO_2 \rightleftarrows H_2CO_3.$$

The water solution has a pleasantly sharp taste, hence its use as plain soda water. One might realize that the acid is weak by reflecting that the moisture and carbon dioxide of the lungs certainly do not injure the tissues of the lungs as would be the case if carbonic acid were a strong acid.

Carbonates and Bicarbonates.—Passage of carbon dioxide into a solution of a base yields carbonates or bicarbonates, depending on the relative amounts of carbon dioxide used. The carbonic acid formed is simply neutralized by the base:

$$(1)\ 2\,NaOH + H_2CO_3 \longrightarrow 2\,H_2O + Na_2CO_3,$$

$$(2)\ Na_2CO_3 + H_2CO_3 \longrightarrow 2\,NaHCO_3.$$

Reaction (1) becomes (2) when an excess of carbon dioxide is bubbled through the solution. The difficulty is in knowing when to stop addition of carbon dioxide for reaction (1). If the "normal" salt, Na_2CO_3, is required, a simple device is to divide the given solution of the base into two equal parts, saturate one part, with the gas (which insures the formation of the bicarbonate $NaHCO_3$), and then mix the two solutions. This means the addition of a number of molecules of the base equal to the number of molecules of the bicarbonate:

$$NaOH + NaHCO_3 \longrightarrow H_2O + Na_2CO_3.$$

Excess of carbon dioxide in soil waters dissolves limestone by formation of the soluble calcium bicarbonate ($CaCO_3 + H_2CO_3 \longrightarrow Ca(HCO_3)_2$). The water then becomes "hard."

All carbonates are insoluble except those of the sodium group. Thus an easy way to precipitate the insoluble ones is to add any soluble carbonate to a solution of any salt of the desired metal.

$$BaCl_2 + Na_2CO_3 \longrightarrow BaCO_3 + 2\,NaCl.$$

Some carbonates are formed by direct union of carbon dioxide and a metallic oxide:

$$CaO + CO_2 \longrightarrow CaCO_3.$$

The normal carbonates of the sodium group react with water to form very strongly basic solutions (salts of a strong base and a weak acid) while the bicarbonates suffer very little hydrolysis. All bicarbonates decompose on heating into carbonates, water, and carbon dioxide:

$$2\,NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2.$$

Uses of Carbon Dioxide.—The Solvay process of making sodium carbonate and sodium bicarbonate requires 500,000 tons of carbon dioxide annually. Since this industry also uses lime it is the best economy to burn limestone in a limekiln and thus secure both carbon dioxide and calcium oxide. There is no need of liquefying the gas for this industry.

The soft-drink industry in America uses 90 per cent of the 60,000,000 pounds of *liquid* carbon dioxide prepared each year. Although some carbon dioxide is collected from fermentation industries, most of the amount liquefied is made by burning clean coke. The flue gases are passed through a solution of Na_2CO_3, which changes to $NaHCO_3$, thus absorbing CO_2. On heating, the $NaHCO_3$ breaks down into Na_2CO_3 and CO_2, the latter product ready for liquefaction. The heat from combustion of the coke is used for power to compress the carbon dioxide. One pound of coal is required to produce one pound of liquid carbon dioxide. The gas is useful in fire extinguishers, where it is formed when needed by the action of sulfuric acid on a dilute solution of sodium bicarbonate. Carbon dioxide, generated in the dough is the chief leavening agent used by the baker.

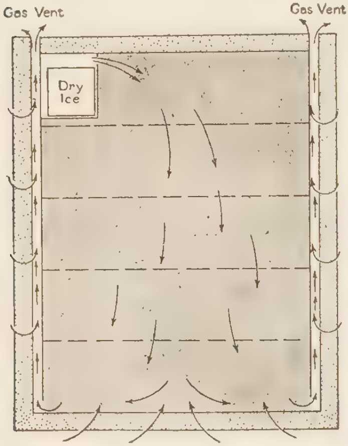


FIG. 46.—Dry-ice refrigeration. The dry, cold, healthful carbon dioxide gas which evaporates from Dry-Ice gradually fills the box. As it is warmed it rises between the double walls, escaping at the top. Heat leaking through the walls of the box is caught by this current of carbon dioxide and quickly carried out—thus never reaching the interior of the box.

"Dry ice" is a trade name for the blocks of highly compressed carbon dioxide snow now being used as a refrigerant. It may possibly compete with water ice for use in refrigeration cars because of the saving in freight, labor of repeated icings and the advantage of absence of water. In properly insulated boxes a large block of this solid carbon dioxide loses only ten per cent of its weight (by evaporation, not by melting) in 24 hours.

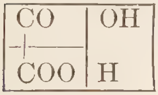
Carbon Monoxide, CO.—This colorless, poisonous, almost odorless gas is formed by burning carbon with an insufficient supply of air:

$$2\,C + O_2 \longrightarrow 2\,CO.$$

Stoves too closely damped may allow escape of some of this dangerous gas into the house. The blue flame flickering over a bed of red hot coals is due to the final burning of carbon monoxide into the dioxide. The dioxide formed in the lower layers is reduced by the hot carbon above. Access of air to the surface of the fuel completes the combustion.

$$CO_2 + C \longrightarrow 2\,CO.$$

A convenient laboratory method of preparation of the monoxide is to heat oxalic acid crystals with concentrated sulfuric acid, which merely extracts the elements of water. This removal of some of the atoms from each molecule causes a general collapse. Among the fragments are carbon monoxide and dioxide. Bubbling the mixture of the two gases through a solution of sodium hydroxide removes the dioxide. (Why?)



$$\boxed{\begin{array}{c|l} \text{CO} & \text{OH} \\ \cline{1-1} \text{COO} & \text{H} \end{array}} \longrightarrow CO + CO_2 + H_2O \text{ (taken by the sulfuric acid).}$$

A better laboratory method of making carbon monoxide is to allow formic acid to drop slowly into concentrated sulfuric acid. Formic acid loses the elements of water to the concentrated sulfuric acid:

$$HCOOH \longrightarrow H_2O + CO.$$

Great care must be used in working with carbon monoxide. Alexander Smith states that 1 vol. in 800 vol. of air is fatal if breathed for 30 minutes. A gas mask is now made containing a catalyst ("Hopcalite") that brings about the oxidation of carbon monoxide into the harmless dioxide.

In tests of the exhaust of a small 23 horsepower automobile engine it has been found that it discharged approximately 25 cubic feet of gas per minute, samples of which gave an average of 6 per cent carbon monoxide, or 1.5 cubic feet of deadly carbon monoxide gas per minute. Of course large engines will give off more. Now a ratio of 15 parts carbon monoxide to 10,000 parts of air is considered a dangerous concentration to be exposed to for a considerable time; and the small 23 horsepower engine in "warming up" and giving off over one cubic foot of carbon monoxide per minute would contaminate the air of a small closed garage, 10 by 10 by 20 feet, to the danger point in about three minutes.

Carbon monoxide is a colorless, tasteless, and almost odorless gas. Its poisonous action depends on the fact that it has a much greater affinity for the hemoglobin of the blood than has oxygen—hemoglobin attracting carbon monoxide about 300 times as strongly as it does oxygen. By combining with carbon monoxide, the hemoglobin of the red blood corpuscles is prevented from giving up its oxygen to the tissues. Death results from paralysis of the respiratory apparatus.

The attack of carbon monoxide poisoning comes on insidiously, and consciousness is gradually lost. Even though the victim may become aware of the danger, he is often unable to escape from it because of the great loss of motor power (*United States Public Health Service*).

In determining the amount of carbon monoxide in air, or in other gases, use is made of the reaction:

$$5\ CO + I_2O_5 \longrightarrow 5\ CO_2 + I_2.$$

The free iodine is readily determined by its loss of color in reaction with sodium thiosulfate.

An extensive study of the carbon monoxide concentration (from automobile exhaust gases) in congested thoroughfares of many large cities showed an average of about 0.8 part in 10,000, not a dangerous condition. The higher concentration, two parts carbon monoxide in 10,000 parts of air, occasionally found, produces a mild to moderate headache after several hours exposure.

A safety device developed by the Bureau of Mines for use in the Holland Tunnel under the Hudson is an automatic carbon monoxide recording machine, which rings a bell and flashes a danger light when the gas becomes more concentrated than 4 parts in 10,000. Then immediate steps can be taken to increase the circulation of air.

Carbon monoxide is a good reducing agent, extracting oxygen from hot metallic oxides:

$$(1)\quad CuO + CO \longrightarrow Cu + CO_2,$$
$$(2)\quad Fe_2O_3 + 3\ CO \longrightarrow 2\ Fe + 3\ CO_2.$$

Reaction (2) is a most important step in the extraction of iron from its ores in the blast furnace. The monoxide unites with sulfur and also with some hot metals, especially nickel and iron. When chlorine and the monoxide are passed over animal charcoal (as a catalyst), the famous poison gas, ***phosgene,*** or carbonyl chloride, is formed:

$$CO + Cl_2 \longrightarrow COCl_2.$$

wed

The Cycle of Carbon in Nature.—All the vast amount of carbon dioxide thrown into the atmosphere by processes of combustion, of decay, fermentation, and animal respiration, is taken up by plants as a valuable food. In the sunlight chlorophyll, the green coloring matter of leaves, is formed and this catalyzes the following reaction:

$$6\ CO_2 + 5\ H_2O \longrightarrow C_6H_{10}O_5 + 6\ O_2.$$

This $C_6H_{10}O_5$ is starch, or cellulose, with molecules containing a large multiple of this formula. The admirable perfection of nature's work is evident from the equation. Not only do plants purify the air but they return all the oxygen of the carbon dioxide to the free atmosphere as oxygen. The woody material of plants actually comes from the air and the water of the sap. When this wood is burned or decays or the starchy foods are eaten, all the carbon dioxide given off makes the same cycle.

Exercise 4.—Diagram the Carbon Cycle (see Nitrogen Cycle, Chapter XXIV).

Phosgene, $COCl_2$.—This dangerous gas has been mentioned under carbon monoxide. It is a colorless liquid below 8°.

$$CO + Cl_2 \longrightarrow COCl_2.$$

Although used as one of the most effective "war gases," it can also be made the starting point in the manufacture of valuable dyes.

Exercise 5.—What relation has urea to the cycle of nitrogen in nature?

Other Carbon Compounds

Carbon Tetrachloride, CCl_4.—This is a colorless liquid (boiling at 77°). It is made commercially by passing dry chlorine into carbon disulfide in the presence of a little iodine as catalyst:

$$CS_2 + 3\ Cl_2 \longrightarrow S_2Cl_2 + CCl_4.$$

The less volatile sulfur monochloride is left behind on distilling off the carbon tetrachloride. The latter, being non-inflammable, is much used as a fire extinguisher. The Pyrene cylinders so common in homes and laboratories contain this liquid. It has been contended that a dangerous amount of phosgene is formed when carbon tetrachloride, and water meet in a fire. Carbon tetrachloride is also a safe solvent for fats, oils, and greases. "Carbona," used in cleaning grease spots from clothing, contains enough of it to make the mixture safe.

Exercise 6.—Of what commercial value is sulfur monochloride? (See chapter on Sulfur.)

Exercise 7.—Starting with free carbon how could you make carbon tetrachloride?

Carbon Disulfide, CS_2.—Carbon disulfide is a heavy, volatile, inflammable liquid possessing a high index of refraction. It has a mild odor when pure, but when impure offends with a very unpleasant odor. The manufacture is simple. Dry charcoal and sulfur are fed into an electric furnace and react in absence of air. (Why absence of air?) The carbon disulfide vapor is condensed as it leaves the furnace:

$$C + 2\,S \longrightarrow CS_2.$$

As a solvent for rubber, sulfur, iodine, and other substances, it has value. Much of it is used in killing rats, mice, ants, and prairie dogs. A little poured into an obnoxious ant hill will be found very effective. Since it is highly inflammable, igniting at a little above 200°, caution must be used when the liquid is applied in buildings. It is dangerous because it vaporizes at low temperature and the vapors form an explosive mixture with air.

Calcium Carbide, CaC_2.—Calcium carbide is prepared in the electric furnace from lime and coke:

$$CaO + 3\,C \longrightarrow CaC_2 + CO.$$

It looks like a porous gray stone, but possesses the valuable property of reacting with water to form acetylene gas:

$$CaC_2 + 2\,H_2O \longrightarrow C_2H_2 + Ca(OH)_2.$$

Calcium carbide is of very great consequence already and bids fair to multiply its usefulness many times. As the starting point for the manufacture of calcium cyanamide, which itself is a valuable fertilizer and a source of ammonia, nitric acid, and explosives, we already know of its economic and military importance. Acetylene will be discussed later and interesting possibilities in its development will be pointed out. Robert Hare, a brilliant pioneer among American chemists, really made the first electric furnace the world ever saw (although unfortunately not much of the world saw his work). With this furnace he made the first calcium carbide, but the world gave little attention to it. Although this was well over a century ago, this substance was forgotten until the Cowles Electric Smelting and Aluminum Company in 1885 made some by accident and observed that when moistened an inflammable gas (acetylene) was given off. Later the Canadian chemist, Thomas Willson, put calcium carbide on the list of important commercial products.

Carborundum, SiC.—The Cowles Company in 1885 also prepared carborundum in their electric furnace but did not understand what the product really was. Acheson, of graphite fame, deserves the credit of "discovering" the substance in 1891. His first device for electric heating of clay and charcoal was crude, but he secured beautiful blue and black iridescent crystals which he was able to sell as "gems" at $560 a pound. Soon he made them in ten-ton batches—and the price fell. A bank of coke and sand which furnish the essential elements is built up with sawdust to make the mass porous, and salt, to form fusible products with the impurities. On passage of a heavy electric current through the mass, the heat of resistance brings about the desired reaction (Fig. 47):

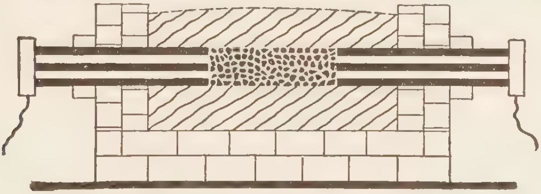


FIG. 47.—Carborundum furnace.

$$3\,C + SiO_2 \longrightarrow SiC + 2\,CO.$$

Only the diamond is harder than carborundum, so this compound is the greatest abrasive known. Pulverized and mixed with clay or other material as a binder, it is shaped into cutting wheels and whetstones and then baked to harden the binder. The advent of carborundum was of enormous industrial importance. With this cheap and powerful abrasive tools were sharpened, metals polished, stone polished, leather finished, glass polished and beveled, buttons shaped—all with far greater speed than was possible before. Carborundum is decomposed at 2240°, the silicon volatilizing and the carbon remaining as graphite.

Cyanogen, C_2N_2.—When mercuric cyanide is heated, cyanogen, a colorless, poisonous gas, with an odor resembling peach kernels is liberated.

$$Hg(CN)_2 \longrightarrow Hg + C_2N_2.$$

Cupric cyanide decomposes almost as rapidly as it forms, yielding cyanogen and cuprous cyanide.

$$2\ Cu(CN)_2 \longrightarrow 2\ CuCN + C_2N_2.$$

Cyanides, Cyanates, and Thiocyanates.—The cyanides are salts of the very weak but intensely poisonous hydrocyanic acid (HCN), sometimes called prussic acid. When sodium cyanide, for example, is treated with dilute sulfuric acid, the volatile hydrocyanic acid escapes.

The cyanates are prepared by oxidizing a cyanide with a heated metallic oxide.

$$PbO + KCN \longrightarrow Pb + KCNO.$$

By warming a solution of ammonium cyanate Wöhler in 1828 brought about a rearrangement of the atoms and obtained urea, the first organic compound ever made outside of a living animal or plant body.

The thiocyanates form a series parallel to the cyanates with sulfur atoms in place of oxygen atoms. On boiling sulfur with a solution of a cyanide the sulfur is added to the molecule.

$$KCN + S \longrightarrow KCNS.$$

EXERCISES

✓8. What is the difference between carborundum and calcium carbide?

✓9. Distinguish between carbon black and lampblack. Which is the better and why?

10. What is the American process of making the carbon dioxide which is to be liquefied for the soda-fountain trade? Why does Europe use another process?

11. What substance in a gas mask catches carbon monoxide?

12. What volume of oxygen would be required to burn 75 liters of carbon monoxide? What volume of carbon dioxide would be formed?

13. Suppose you wished to prepare 14.5 liters of CO_2 by the action of hydrochloric acid on marble. What weight of hydrogen chloride and marble would be required?

14. A compound has the following composition: Carbon 26.5 per cent, Hydrogen 2.2 per cent, Oxygen 71.2 per cent. What is the compound?

15. What volume of acetylene at 20° and 740 mm. is obtained by the action of water on 6.5 g. calcium carbide?

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"Solid Carbon Dioxide, A New Commercial Refrigerant," *Ind. Eng. Chem.*, *19*, 192, (1927).

"The Romance of Carbon" (Little), *Ind. Eng. Chem.*, *18*, 444, (1926); also *Jour. Chem. Ed.*, *5*, 1321, (1928).

7. Carbon black - carbon of flame or is soot.
Lamp-black - " " smoky flame of tars & oils
C.B. best - used for printer's ink & rubber good
better carbon

8. Carborundum SiC. ~~[illegible]~~ most useful abrasiv known.
Calcium carbide CaC_2 reacts with water to form acetylene

0. Dissolving CO_2 in H_2O and putting more into solution under 10 ~~[illegible]~~ atmosphere pressure.

CHAPTER X

MOLECULAR AND ATOMIC WEIGHTS

The student has been taught to use exact atomic weights and has all along wondered how we arrived at such values. He has been promised an explanation and it is now in order.

Dalton, Gay-Lussac, Avogadro.—In 1805, just after the publication of Dalton's atomic hypothesis, Gay-Lussac found by laboratory experiment that in any chemical reaction the volumes of all gases concerned stand to each other in the ratios of small whole numbers. Avogadro in 1811 sought to explain this and other facts by his famous hypothesis that ***equal volumes of all gases,*** under the same conditions of temperature and pressure, ***contain the same number of molecules.***

Development of Exact Weights.—From the above it is evident that if we weigh equal volumes of gases under like conditions we get weights that are in the same ratios as the weights of *single molecules.* In other words, we can get the relative molecular weights of all gases. (Solids must be handled differently.)

If you were doing this, and knew nothing of our present system of atomic and molecular weights, what gas would you naturally select as a standard with which to compare all others? You would probably select the lightest gas—hydrogen.

Since these molecular weights are only relative, what would you select as the weight of *one molecule* of hydrogen? As the lightest molecule known you would doubtless suggest "1" as the weight of a hydrogen molecule. Now the oxygen molecule actually weighs 16 times as much (1 liter of oxygen is 16 times as heavy as 1 liter of hydrogen). Therefore, on this basis (molecular weight of hydrogen = 1), the molecular weight of oxygen = 16. On the same basis the molecular weight of water vapor = 9.

As it turned out, the attempt to set 1 as the standard molecular weight of hydrogen introduced troublesome fractions. Gay-Lussac, early in the last century had observed that one volume of hydrogen united with one volume of chlorine to form two volumes of hydrogen chloride.

$$\begin{array}{ccccccc} H_2 & & Cl_2 & & HCl & & HCl \\ \boxed{1\text{ vol.}} & + & \boxed{1\text{ vol.}} & \longrightarrow & \boxed{1\text{ vol.}} & + & \boxed{1\text{ vol.}} \\ \text{hydrogen} & + & \text{chlorine} & & \multicolumn{3}{c}{\text{hydrogen chloride}} \end{array}$$

But by Avogadro's theory the two volumes of hydrogen chloride contained twice as many molecules as the one volume of hydrogen. Now *every* molecule of hydrogen chloride contains *some* hydrogen. There is only one way for a given number of hydrogen molecules to be represented in twice that number of hydrogen chloride molecules. Each hydrogen molecule splits into two parts and each half molecule is found in each molecule of hydrogen chloride. In other words there are two atoms of hydrogen in a molecule of hydrogen.

Gay-Lussac also observed that one volume of oxygen unites with two volumes of hydrogen to form two volumes of water vapor. By logic similar to that used above he deduced (as you may also) that there must be two atoms in one molecule of oxygen, the formula of which is then set as O_2.

It follows, also, that if the hydrogen molecule contains two atoms, the atomic weight of hydrogen can be only half the molecular weight and the formula must be H_2. Naturally it was decided to call the weight of the molecule 2, so that the smallest unit taking part in chemical reactions, the hydrogen atom, could be set as 1. Since all these values are relative, there was justification in making the standard molecular weight a convenient value.

Finally, the scientific world agreed that rather than set the weight of a molecule of hydrogen at exactly 2, which forced the relative value for the oxygen molecule 31.746 it would be better to set the molecular weight of oxygen as the standard and call it exactly 32, letting the molecular weight of hydrogen take its relative value of 2.016 (and the atomic weight 1.008). Since hydrogen unites with few elements and oxygen with nearly all, fewer experimental errors are involved with the oxygen standard.

This logic gives the number of atoms in one molecule of elementary gases but not the number in a molecule containing two or more elements.

Cannizzaro's Suggestions.—Avogadro's useful theory was not taken seriously until long after his time. Scientists were sadly confused as to the distinction between atomic weights and molecular weights. Then in 1860 Cannizzaro, another Italian, offered a few suggestions that cleared away the confusion. He insisted that molecules of elements were made up of atoms of the same kind and that molecules of compounds were made up of atoms of different kinds. To develop a system of atomic weights he suggested that:

1. The molecular weights of all the volatile compounds of the element studied should be determined.

2. These compounds should all be analyzed and the part of each molecular weight due to the particular element determined.

3. The smallest weight of the element found in any of the molecular weights of its compound should be selected as the atomic weight.

Following is given a short table of oxygen compounds based on the present accepted standard of 32 for the molecular weight of oxygen. From the weights of equal volumes of oxygen and water vapor, for example, it was learned that the molecular weight of water must be 18.016. By analysis it was found that almost exactly 8/9 of any amount, even a single molecule of water, is oxygen. Consequently 8/9 of 18.016, or 16 parts of this total molecular weight of 18.016 is due to oxygen. The values for other oxygen compounds were developed in the same manner.

A Few of the Many Thousand Oxygen Compounds

Substance	Molecular Wt.	Part of Mol. Wt. Due to Oxygen (by analysis)
Oxygen	32.0	32
Water	18.016	16
Carbon monoxide	28.0	16
Carbon dioxide	44.0	32
Sulfur dioxide	64.064	32
Nitrogen trioxide	76.016	48
Nitric oxide	30.008	16
Phosphorus pentoxide	142.054	80

If the complete table of many thousand oxygen compounds were listed in this way, you would note that the smallest part of any molecule due to oxygen is 16. Is it not practically certain that out of thousands of chances nature would put just one atom of oxygen in some molecules? If so, does not the smallest amount of oxygen (16) in any molecule represent the weight of one atom? Therefore should not the *atomic weight* of oxygen be 16? Gay-Lussac arrived at the same conclusion by a rather limited method (already given).

Let us deduce the formula of water: analysis would show that about 8/9 of the water molecule is oxygen. This fraction of 18.016 = 16. Since the weight of one atom of oxygen = 16 (as just shown), there must be only one atom of oxygen in the molecule of water. The part of the molecular weight, 18.016, due to hydrogen is, of course, 2.016 or the weight of two atoms, and the formula must be H_2O.

Limited Portion of a Table from Which Atomic Weights Were Selected

Substance	Molecular Weight	Weights of Elements in Molecular Weights of Compounds							
		Hydrogen	Chlorine	Oxygen	Carbon	Phosphorus	Nitrogen	Molecular Formula (?)	
Water	18.016	2.016		16				H_2O	
Hydrogen chloride	36.468	1.008	35.46					HCl	
Methane	16.032	4.032			12			CH_4	
Acetylene	26.016	2.016			24			C_2H_2	
Ethylene	28.032	4.032			24			C_2H_4	
Benzene	78.048	6.048			72			C_6H_6	
Carbon tetrachloride	141.84		141.84		12			CCl_4	
Carbon dioxide	44.			32	12			CO_2	
Phosphorus pentoxide	142.054			80		52.054		P_2O_5	
Ammonia	17.024	3.024					14.008	NH_3	
Phosphorus trichloride	137.41		106.38			31.027		PCl_3	
Alcohol	46.048	6.048		16	24			C_2OH_6	H_6C_2
Ether	74.08	10.08		16	48			C_4OH_{10}	$H_{10}C_4$
Nitrogen trioxide	76.016			48			42.024	N_3O_4	
Nitric acid	63.016	1.008		48			14.008	HNO_3	

Exercise 1.—With the logic used in connection with the selection of the atomic weight of oxygen and the development of H_2O as the correct formula for water, proceed to select from the table above the atomic weights of the six elements used and calculate the formulas of the compound named in the table.

The Molar Volume.—Since we have decided on 32 as the *molecular* weight of oxygen, it might be useful to know what volume the formula weight of 32 g. would occupy. One liter of oxygen weighs 1.429 g., so $\frac{32}{1.429} = 22.4$, the number of liters occupied by 32 g. of oxygen. We can, for convenience, imagine a box holding exactly 22.4 liters (Fig. 48). This is nearly one cubic foot. If it is filled with oxygen or any other gas under standard conditions, the weight of the contents in grams must be the *formula weight* of that gas, since that is true for oxygen. By Avogadro's law this box must hold the same number of molecules of any gas, so the weights vary as the weights of single molecules. The box filled with hydrogen weighs 2.016 g., therefore the molecular weight of hydrogen is 2.016. The molar volume of ammonia (NH_3) weighs 17 g. Obviously the molecular weight of ammonia is 17.

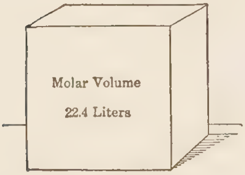

Fig. 48.—The molar volume is approximately one cubic foot.

In actual practice we should find it awkward to weigh 22.4 liters. We should simply weigh (get the density of) any convenient volume, perhaps 200 cc. and calculate the weight of 22.4 liters.

Dumas devised a simple method of measuring gas density. He used a bulb with a stopcock attached. After finding the exact volume of the bulb by filling with mercury and weighing it was then weighed filled with air. Knowing the volume of air in the bulb (and the density of air) it was a simple matter to calculate the weight of the air alone. Subtracting this weight from the weight of the bulb filled with air gave the weight of the bulb alone, a method equivalent to weighing an evacuated bulb. Finally the bulb was weighed after filling with the gas whose molecular weight was desired. By subtracting the weight of the empty bulb from the weight of bulb plus this gas, the weight of the given volume of gas was found. From this it was easy to calculate, by proportion, the weight in grams of 22.4 liters. This number represented the molecular weight. Of course corrections to 0° and 760 mm. were made. A very volatile liquid can be examined by placing the bulb containing some of it in a heated water bath and when only its vapor remains closing the stopcock and weighing.

Exercise 2.—What is the molecular weight of a gas 150 cc. of which weighs 0.235 g. under standard conditions?

Exercise 3.—A Dumas bulb of 300 cc. volume was filled with vapor from an easily volatilized liquid at 45°. The barometer read 740 mm. What was the molecular weight of the liquid if the gas weighed 1.25 g.?

Exercise 4.—The density of a certain gas referred to air is 1.85. (1 liter of air, standard, weighs 1.293 g.) What is the molecular weight of this gas?

Note: The weight of one liter of any gas in grams can be calculated in a minute by dividing its molecular weight by 22.4. For example, 22.4 l. of oxygen (G. M. V.) weighs 32 g. Therefore 1 liter weights $\frac{32}{22.4} = 1.429$ g.

Exercise 5.—Calculate the weight of 1 liter of nitrogen (N_2); of 300 cc. of chlorine (Cl_2); of 1500 cc. ammonia (NH_3).

The molecules of most, but not all, *elementary* gases are diatomic. For example a molecule of chlorine is Cl_2 and of nitrogen N_2. Yet mercury vapor is monatomic and its *molecular* formula is Hg. Zn is the molecular formula for zinc vapor. A few rare gases, such as helium, neon, and argon, are monatomic. Temperature affects some molecular structures to a marked degree. At 448° I_2 is the correct formula of iodine vapor, but at 1700° iodine must be written I. At 193° sulfur vapors are represented by S_8, but at 1719° by S_2. At 193° the G. M. V. (22.4 liters) of sulfur vapor (corrected to 0° and 760 mm.) weighs 256 g. This means that the molecular weight at that temperature is 256. Since one sulfur atom weighs 32, there must be eight atoms in the molecule.

Exercise 6.—What must one liter of sulfur vapor weigh at 1719°?

Exercise 7.—The use of molecular formulas may seem puzzling at first, but it soon becomes a real convenience. The following example will show this: when limestone is heated to white heat in the kiln it forms quicklime and carbon dioxide:

$$CaCO_3 \rightarrow CaO + CO_2.$$

How many liters of carbon dioxide can be liberated from 25 g. of limestone? The answer is found at once. The formula $CaCO_3$ represents a definite quantity, the gram-molecular weight (one "mole") or 100 g. So does CO_2 represent one mole. But the molecular weight in grams of any gas occupies 22.4 liters. (See Molar Volume.) Now if 22.4 liters of carbon dioxide are released from 100 g. of limestone, 1 g. will release $\frac{22.4}{100}$ liters and 25 g. will release $\frac{25 \times 22.4}{100}$, or 5.6 liters.

$$\begin{array}{l} CaCO_3 \rightarrow CaO + CO_2, \\ 100 \text{ g.} \rightarrow 56 \text{ g.} + 44 \text{ g. (or 22.4 l.).} \end{array}$$

Exact Atomic Weights.—Deviations from the gas laws make Avogadro's law only a very good approximation. But equivalent weights may be determined with marvellous accuracy, as shown by the brilliant atomic weight determinations of the American chemist, T. W. Richards.

With the molecular weight of some compound of a given element, a correct analysis of that compound, and the exact equivalent weight of the element, it is easy to determine the exact atomic weight desired.

With the "mass-spectrograph" Aston has determined atomic weights with an accuracy of one part in 1000.

There is always a much greater experimental error in determining the density of a gaseous compound (and hence its molecular weight) than in determining the equivalent weight of an element. For example, suppose 22.4 liters of the volatile chloride of a new element "E" are found to weigh 116 g. This fact places the molecular weight at 116. By analysis of this chloride we learn that 40 per cent of it is "E" and 60 per cent of it chlorine, that is, they unite in the proportion 40 : 60. In 100 g. of the compound there are 40 g. of E, and 60 g. of chlorine.

Our system of "equivalent weights" is built on the number of grams of any element equivalent to 1.008 g. of hydrogen or 8 g. of oxygen, or 35.46 g. of chlorine. To get the exact equivalent weight of "E" we need only calculate (from the 40 : 60 ratio) the weight of E equivalent to 35.46 g. of chlorine. This is done with the proportion

$$40 \text{ g. E} : 60 \text{ g. } Cl_2 = X \text{ (equiv. wt. of E)} : 35.46 \text{ (equiv. wt. of } Cl_2\text{)}$$
$$X = 23.64, \text{ the equiv. weight of E.}$$

As stated on page 14 the atomic weight of an element is the same as the equivalent (or combining) weight or at most a small multiple of it. Thus we know that 23.64 or 2 × 23.64 or 3 × 23.64, etc., must be the *exact* atomic weight of E. Since the molecular weight of this chloride has been found to be 116 (within the limit of experimental error) and 40 per cent of this weight is due to E, it is evident that 0.40 × 116 or 46.4 of the total molecular weight of 116 is due to E. This we shall call the weight of one atom unless later we find another compound in which the part of the molecular weight due to E is less than 46.4. At a glance we see that 46.4 is nearly but not quite 2 × 23.64. But for the greater experimental error in determining the molecular weight of the chloride from the density of the gas, this value would be exactly 2 × 23.64. Consequently we accept 47.28 (2 × 23.64) as the exact atomic weight of E. To make the illustration clearer we purposely exaggerated the probable error in determining the weight of 22.4 liters of the volatile chloride.

Since the part of the molecular weight due to chlorine is about 60 per cent of 116 or 69.6, there must be two atoms of chlorine in each molecule and the formula of the chloride must be ECl_2. The valence of E is 2.

EXERCISE 8.—Suppose 22.4 liters of a volatile bromide of a new element weigh 203 g. and 60 per cent of the compound is found, by analysis, to be the new element "E." What is the atomic weight of E, its valence and the formula of the compound?

Law of Dulong and Petit.—In 1818 Dulong and Petit observed that the product of the atomic weight of an element by its *specific heat* is equal to about 6.4. (The specific heat of a substance is the number of calories required to raise the temperature of one gram 1° C. The specific heat of water is almost the highest of all, 1.0, while that of copper is 0.1.) The law does not hold accurately but it is sufficient to settle many disputes, and invaluable in determining the atomic weight of an element which has no volatile compound. Carbon, boron, and silicon deviate widely from this law.

at. wt. × sp. heat = atomic heat
Al, 0.209 × 27 = 5.6
Zn, 0.093 × 65.4 = 6.1
Cu, 0.0923 × 63.6 = 5.88
Fe, 0.1098 × 55.5 = 6.12
Ag, 0.056 × 107.88 = 6.12
Hg, 0.0335 × 200 = 6.7

Analysis of silver oxide (93.1 per cent silver and 6.9 per cent oxygen) indicates that 215.76 g. of silver combine with 16 g. of oxygen or 107.88 g. with 8 g. As we have learned before, the atomic weight is either the same as the combining weight or some multiple of it but this does not decide between such possible atomic weights as 107.88, 2 × 107.88, 3 × 107.88, etc. Dulong and Petit's law, approximation though it is, makes the choice for us.

$$\text{Atomic weight of silver} \times 0.056 = 6.2$$
$$\therefore \text{Atomic weight} = 110, \text{approximately.}$$

Obviously this indicates the more accurately determined value, 107.88 rather than 215.76, etc. The formula must be Ag_2O.

Specific heat for elements of high atomic weight is proportionally less than for those of lower atomic weight. There are, of course, fewer atoms in one gram of a heavy element than in one gram of a lighter element. Consequently, equal amounts of heat are required to raise equal numbers of atoms one degree.

EXERCISES

9. A certain compound contains, by analysis, 29.40 per cent of calcium (Ca), 23.56 per cent of sulfur (S), and 47.04 per cent of oxygen. The molecular weight is 136.2. Using these values and the table of atomic weights, calculate the formula. See the discussion at the first of this chapter.

10. When 22.4 liters of water vapor (estimated under standard conditions) condense, how many cubic centimeters of liquid water are formed?

11. The "Avogadro Number" represents the actual number of molecules of any gas in 22.4 liters (standard conditions). This number is 6.06×10^{23} molecules. Calculate the actual weight of one of these minute, invisible molecules.

12. How could you determine the number of atoms in a molecule of chlorine?

13. Does the molar volume of water (weighing 18 g.) refer to liquid or gaseous water? The molar volume is nearly one cubic foot.

14. If 1 liter of nitrogen at 0° C. and 760 mm. weighs 1.251 g. what is the molecular weight?

15. Find the molecular weight of a gas, of which 250 cc. at 18° and 752 mm. weigh 2.5 g.

16. The density of a gas is 2.3 as compared with air = 1. What is its molecular weight?

17. What will be the volume occupied by 2 g. of carbon tetrachloride (Molecular weight 153.84) in the vapor state at 0° and 760 mm.?

18. The specific heat of an element in the solid state is 0.245. Its chloride contains 25.54 per cent of the element and 74.46 per cent of chlorine. What is the atomic weight of the element? (Hint: Calculate the approximate atomic weight by the rule of Dulong and Petit. Then calculate weight of element combined with 35.46 g., the equivalent weight, of chlorine.)

19. Dumas made 59.3765 g. of carbon dioxide by burning 16.192 g. of carbon. Accepting the correct atomic weight of oxygen as 16, calculate the atomic weight of carbon.

REFERENCES

"Methods of Determining Avogadro's Number" (Sunier), *J. Chem. Ed.*, *6*, 299 (1929).

CHAPTER XI

SOLUTIONS

A solid and a liquid may be so intimately mixed that separate particles of the solid are no longer seen. With certain reservations to be given later we may call this mixture a ***solution.*** Salt water is a good illustration. If the mixture is less intimate, so that minute particles of the solid may be seen with the microscope, we may call it a ***suspension.*** Two liquids may also mix so completely as to deserve the term ***solution.*** If less thoroughly mixed, minute droplets of one liquid suspended in the other may be seen. Such a mixture is called an ***emulsion.*** Milk is an example.

A crystal of potassium permanganate half the size of a grain of wheat gives a perceptible pink color to every part of twenty liters of pure water. Each cubic centimeter contains about twenty drops, so in twenty liters, or twenty thousand cubic centimeters, there must be 400,000 drops. Each drop contains $\frac{1}{400,000}$ of the weight of the fragment of permanganate which weighed possibly 0.02 g. Nor is this the limit of such subdivision. Try the same experiment with a dye such as methylene blue or malachite green. Start with 0.01 g. in one liter. Pour 10 cc. of this into a liter flask and fill it with pure water. The concentration is now only $\frac{1}{100}$ that of the first solution. Take out 10 cc. of this second solution, dilute to a liter as before, and continue until the color is barely perceptible. Now calculate the weight of dye in a single drop. With a needle point you can divide a drop into ten visible portions.

Solutions are non-settling and are homogeneous to the eye. Suspensions or emulsions settle, sooner or later, and are not homogeneous under severe tests. In a true solution the particles of dissolved substance are single molecules or, at most, groups of a few molecules. Consequently ***a solution is a homogeneous molecular mixture of substances.*** It should be noted that the proportions of the components of a solution (sugar and water, for example) may be varied within limits. This distinguishes a solution from a compound.

Solutions might also be defined as homogeneous bodies whose composition is capable of continuous variation, at least within certain limits.

Colloid Solutions.—As just stated, true solutions are approximately molecular dispersions of one substance in others. Dispersions of molecular aggregates larger than the largest single molecules now known, and yet not greater in the smallest dimension than 200 millionths of a millimeter are termed ***colloid dispersions*** or solutions. Coarse suspensions settle quickly but some colloid solutions in water have failed to settle after many years. The dispersion need not always be in a liquid. Ruby glass of one type owes its color to gold aggregates of colloidal size dispersed in solid glass. An entire chapter is later given to a discussion of colloid chemistry.

Types of Solution.—We are most familiar with solutions of solids in liquids, but liquids and gases may also be dispersed in liquids to form solutions. When a beaker of tap water is warmed bubbles of dissolved air may be obtained. Furthermore, solids dissolve in solids and liquids dissolve in solids. Some alloys are mixtures of metals so intimate as to deserve the name solution. A disk of gold was once clamped against a rod of solid lead and kept four years locked in a safe of the Bank of England. At the end of that time thin shavings of lead were cut off and analyzed. The gold had penetrated 7 mm. into the lead, forming a solid solution.

To stretch imagination still farther we may add that gases dissolve in solids. Palladium under certain conditions dissolves over eight hundred volumes of hydrogen.

Hardened steel is probably a homogeneous solid solution of carbon in iron (martensite) but softer steel is a mechanical mixture of pure iron and a carbide of iron.

Some substances dissolve quite simply; others first react with the solvent to form soluble compounds, which then dissolve. Zinc does not really "dissolve in dilute sulfuric acid" but is converted into zinc sulfate which dissolves.

Exercise 1.—To which type of solution does dilute sulfuric acid belong? Ordinary hydrochloric acid from the desk bottle? Ammonia water? Table syrup?

Water is the great solvent, but alcohol, ether, benzene, carbon disulfide, and thousands of other liquids are solvents for various substances. Water does not dissolve fats, yet carbon disulfide does. Sulfur dissolves readily in carbon disulfide, but not in water. Salts usually dissolve in other melted salts.

Although benzene (C_6H_6) and common ether dissolve very few inorganic salts it is possible to make concentrated solutions of lithium perchlorate ($LiClO_4$) and of silver perchlorate in benzene.

Solid Solutions.—Iodine gives solid solutions with benzene (C_6H_6). Now when a solution of iodine in benzene (the common type of solution) is frozen the iodine does not separate, but remains uniformly dispersed, dissolved, in the crystalline benzene, even after many hours at − 80°. But when fluid solutions of iodine in bromoform ($CHBr_3$) or ethylene bromide ($C_2H_4Br_2$) are frozen the uniform violet color soon disappears, and grey iodine crystals are seen. In this instance a solid solution simply did not exist.

The question might well be raised: When copper and aluminum are melted together is a solution formed (solid after cooling), or is a compound of the two metals formed? A definite X-ray spectrum (p. 66) has been found for the compound $CuAl_2$ entirely different from that of either metal. Probably the aluminum and the copper each builds up its own special crystal lattice. Bruni holds that in solid solutions there is a single lattice with some distortion due to interatomic replacements, while compounds are constituted by the reciprocal interpenetration of at least two lattices.

Definitions.—The liquid in which a solid or gas has been dispersed to form a solution is called the ***solvent*** and the substance dissolved the ***solute.*** In the case of two liquids or two solids, each one may be said to be dissolved in the other, though the one present in larger quantity is usually termed the solvent.

By ***concentration*** we mean the amount of solute dissolved by a definite quantity of the solvent, often referred to as so many grams per 100 cc. of solvent (or even per 100 cc. of solution). A solution containing relatively very little of the solute is ***dilute.*** In a ***concentrated solution*** there is a large amount of dissolved substance. Solutions may be made more concentrated (up to a certain limit) by adding more solute, preferably finely powdered, and shaking or stirring some time or by evaporating a dilute solution to remove part of the volatile solvent. Carried to the limit this is ***evaporating to dryness*** (in the case of solids in liquids) and the solute is recovered as a dry solid.

It is often incorrectly stated by the student that a saturated solution is one that contains all it can hold of the dissolved substance. That this is an error is readily proved by the formation of *supersaturated* solutions. Stir powdered sodium sulfate ($Na_2SO_4 \cdot 10\ H_2O$) for some time in water at 30°, making sure that some is left over. Let settle and decant most of the solution into a clean flask, taking care that no fragment of the solid is transferred. Cover the flask to keep out dust and let cool. Now this solution, saturated at 30°, contained all it could hold, or it would have taken up more when it had the chance. After cooling to 15° the solution should throw down part of the solute because, in general, solids are less soluble on cooling. Yet this particular one continues to hold at 15° all it held at 30°. The same thing can be done with photographer's "hypo." We call the solution at 15° *supersaturated* and the natural definition—that it contains *more* than it can hold—is absurd. But toss in a minute fragment of a crystal of sodium sulfate and quickly a beautiful network of crystals radiates from the fragment. The amount thus crystallizing out is the difference between the amounts securely held at 30° and 15°. We now see a more accurate definition.

A ***saturated solution*** is *one which will remain unchanged in concentration if placed in contact with some of the undissolved solute.* It is said to be in equilibrium with excess of solute. That is, when we stir sugar, for example, into water it continues to dissolve until the rate at which the sugar molecules in solution deposit on the lumps of solid sugar just equals the rate at which the solid throws molecules into the solution (Fig. 49). There is then no further change in the quantity in solution, but there is ceaseless activity. If a perfect crystal of alum with a cavity dug in the side is placed in a saturated solution of alum for several days, with no evaporation and no temperature change permitted, it is observed that the cavity fills up but the crystal weighs no more. The whole surface of the crystal has steadily dissolved and steadily been replaced, but in the accustomed regular form without cavities or broken edges.

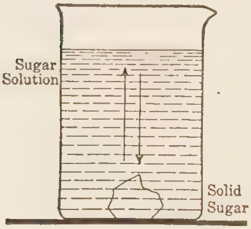

Fig. 49.—Solution equilibrium.

A ***supersaturated solution*** is in an unstable condition and if placed in contact with some of the solid solute it throws down the excess over the amount held by a saturated solution. Therefore it can be stated that a supersaturated solution has a higher concentration than the corresponding saturated solution.

An ***unsaturated solution*** has a lower concentration than the saturated solution.

Exercise 2.—If a clear solution of "hypo ($Na_2S_2O_3$) were given you to test, how could you tell whether it was unsaturated, saturated, or supersaturated?

Water saturated with one substance may still dissolve another just as a box of oranges may take up considerable sand and finally a surprising amount of water.

Measuring Solubility.—Water comes near being the "universal solvent" hunted for by the alchemists. Most so-called insoluble substances dissolve in water to a minute extent at least, as can be shown by electrical conductivity measurements. That glass dissolves noticeably is readily observed by adding powdered glass (greatly increased surface) to water containing a drop or so of the indicator, phenolphthalein. The pink color seen is characteristic of basic solutions containing this indicator. Glass and water react to form a small amount of a base. Even metals dissolve. Water in a copper vessel is slowly sterilized by the minute amount of copper thrown into solution. There are many degrees of solubility. Limestone ($CaCO_3$), called calcium carbonate in its pure form, dissolves to the extent of 0.00013 g. in 100 cc. of water, while 143 g. of potassium hydroxide dissolve in the same quantity of water.

By a "10 per cent solution" we mean one containing 10 grams of solute and 90 grams of water (or solvent).

The ***temperature effect*** on solubility must be considered in any of these quantitative statements. Nearly all solids are more soluble with rise in temperature, but there are a few exceptions, notably some calcium salts of organic acids. (Gases, however, are less soluble with rise in temperature.) Potassium nitrate is seven times as soluble at 70° as at 8°. There can be no accuracy, then, in a solubility statement unless the exact temperature of the measurement is given. This is usually 18° or 20°, the common working temperatures of our laboratories.

To make a solubility measurement we merely determine the number of grams of solute taken up by 100 cc. of water in a saturated solution at a definite temperature. This may be done by slowly stirring the powdered solid into water until no more is dissolved and keeping a record of the weights. There is much chance for error here, as some solids dissolve slowly. It is more accurate to stir in an excess and, after much stirring and settling, to remove an accurately weighed or measured portion of the clear solution and carefully evaporate it to dryness on a steam bath. The loss in weight represents the water and the residue the solute. The results can be calculated as grams per 100 cc. of water (or 100 cc. of solution if preferred). Less time is required if one heats an excess of solid with water at a higher temperature than the one at which the measurement is to be made. The solution is then cooled and held a short time at the exact temperature desired until the excess has deposited and settled. A measured portion is then evaporated to dryness as before.

The solubilities at various temperatures may be plotted in the form of curves using the ordinates to represent the number of grams of solid dissolved by 100 cc. of water. The abscissas represent temperatures.

With the curves on page 142 the solubility at any temperature may be read at a glance. What is the solubility at 18° and 90° of lead nitrate? Of sodium chloride at 77°?

Exercise 3.—Plot points on a solubility diagram according to the following approximate data and then connect these points in smooth curves (or straight lines, as the case may be).

	0°	10°	30°	50°	70°	90°	100°
Potassium alum	6.5 g.	8.0 g	17.5 g.	32.0 g.	113.0 g.		
Ammonium chloride	29.0 g.	33.0 g.	42.0 g.	50.0 g.	60.0 g.	72.0 g.	78.0 g.

Saturate 200 cc. of water with cerium sulfate, $Ce_2(SO_4)_3$, at 0°. Heat to boiling. A mass of crystals separates. The solubility at 0° is 19.09 g. and at 100° C. it is 0.78 g.

Place a small beaker containing 30 cc. of very cold water on a small wet block of wood. Stir in 24 g. of powdered ammonium nitrate. Or better yet add a freshly prepared dry mixture of 100 g. NH_4Cl, 150 g. $Na_2CO_3 \cdot 10\,H_2O$ to 300 cc. of cold water. The latter will lower temperature of the water about 31° C. Why does the beaker freeze to the wood?

Temperature and Volume Changes of Solutions.—The student has already observed the astonishing amount of heat released when concentrated sulfuric acid is mixed with water and he may have observed a marked rise in temperature when anhydrous calcium chloride is dissolved in water. The heat of solution in these cases probably involves an actual chemical reaction between solute and solvent. One gram molecular weight of concentrated sulfuric acid added to a large volume of water releases 39,170 cal. On the other hand one gram molecular weight of ammonium chloride *absorbs* 3880 cal. on dissolving. Many salts produce this cooling effect or, in other words, their heat of solution is negative. This is very marked in the case of potassium iodide. This cooling effect may depend upon changes in the aggregation of water molecules caused by the dissolved substance. Conversely when these salts crystallize from solution heat is given out. When sodium acetate crystallizes from a super-saturated solution, much heat is released. This fact is utilized in one type of hot water bottle, useful for travelers.

As a rule the volume of a solution is less than the sum of the volumes of solute and solvent, but in the case of ammonium chloride and water it is greater. There are a few such exceptions. Gases dissolved in water may increase the volume. One liter of water saturated with ammonia gas increases to 1.580 liters at 14°.

Breaks in Solubility Curves. Transition Points.—Referring to Fig. 50, the chart of solubility curves, we observe a peculiar break, or sharp peak, in the curve for sodium sulfate. Using $Na_2SO_4 \cdot 10\,H_2O$ we find that its solubility increases up to 32.4° and then suddenly decreases. The fact is that at 32.4° this hydrate loses its water of crystallization:

$$Na_2SO_4 \cdot 10\,H_2O \longrightarrow Na_2SO_4 + 10\,H_2O.$$

Above 32.4° the curve represents the solubility of anhydrous sodium sulfate, Na_2SO_4, this salt being less soluble with rise in temperature. In other words this sharp point is the intersection of the two curves for these two crystalline forms of sodium sulfate. Such points, or temperatures, are called ***transition points*** and represent a distinct chemical change.

The temperature at which an abrupt change in any physical property occurs is called a *transition temperature* or point. This may be a change in color, volume, solubility, vapor pressure, crystal shape, etc. It is difficult to determine an exact transition temperature for oxygen-ozone but easy for $Na_2SO_4 + 10\ H_2O \rightleftarrows Na_2SO_4 \cdot 10\ H_2O$ when both salts are in solution.

Exercise 4.—If you were in a hurry to dissolve sodium chloride, would you use hot or cold water?

Exercise 5.—Salt solutions are heavier than water. To dissolve commercial quantities of some solid substance without the expense of stirring or heating, would it be better to place the solid at the bottom of the vat or on a perforated shelf near the top?

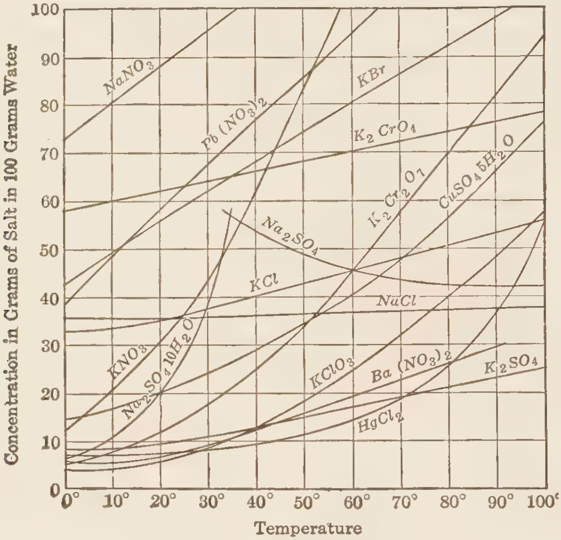

Fig. 50.—Solubility curves.

Solubility of Liquids in Liquids.—Many pairs of liquids mix (dissolve in each other) in all proportions. Water and alcohol, water and sulfuric acid, water and glycerine are examples. But "oil and water" do not mix at all. It is true that an emulsion of minute droplets of oils in water can be made, but these droplets contain thousands of molecules and so are not in true solution. Other liquids dissolve in each other to a limited extent. If ether and water are shaken and allowed to stand, an ether layer rises to the top with a water layer beneath. Analysis shows the presence of a little water dissolved in the ether layer and a little ether dissolved in the water layer. From these illustrations we see that liquids may be ***completely miscible, partially miscible,*** or ***immiscible.***

Exercise 6.—Give an illustration of each type.

Solubility of Gases in Liquids. Henry's Law.—In 1803 Henry observed that at any definite temperature ***the solubility by weight of a gas in a liquid is proportional to the pressure*** of the gas. The volume of gas dissolved with increasing pressure remains constant even though the weight increases. At 0° and 760 mm. only 2 cc. of hydrogen dissolve in 100 cc. of water, while at two atmospheres (1520 mm.) 4 cc. of hydrogen as measured at one atmosphere, dissolve in 100 cc. of water. However, at the new pressure of 2 atmospheres these 4 cc. will be compressed to 2 cc. Ammonia (NH_3) at 0° and 760 mm. dissolves to the extent of 114,800 cc. in 100 cc. of water, but its solubility does not follow Henry's law. In fact, all very soluble gases are exceptions, probably because they react to some extent with water. Certainly ammonia does, forming ammonium hydroxide (NH_4OH). Hydrogen chloride (HCl) is very soluble, while air is but slightly soluble.

With rise in temperature all gases are less soluble in liquids. Warming ammonia water drives off much of the dissolved gas and boiling removes it all. Passing a stream of another gas, say air or steam, through a solution of a gas in water removes the dissolved gas for reasons given in the next section.

Exercise 7.—What weight of ammonia dissolves in 1 l. of water at 0° and 760 mm.?

Exercise 8.—Would Henry's law hold closely for the solubility of hydrogen chloride in water? Of nitrogen?

Law of Partial Pressures.—If a liter of hydrogen and a liter of nitrogen at 760 mm. are forced together in a one-liter vessel, the total pressure becomes two atmospheres and each gas exerts its own part of the pressure (one atmosphere). If mixed in a two-liter vessel, the hydrogen expanding to twice its previous volume could exert only one half of one atmosphere's pressure (Boyle's law). But the sum of this and a corresponding half atmosphere for nitrogen is one atmosphere for the two gases. Each attends to its own pressure as if the other gas were not present.

If a bottle of air is closed with a stopper containing a mercury pressure gauge or manometer, the pressure may be read in millimeters of mercury. Now if a thin bulb of water in the bottle is broken, the release of water vapor inside the bottle adds to the air pressure, as shown by the rise of mercury in the manometer. Such experiments as these led Dalton in 1802 to state that ***in a mixture***

of gases each gas exerts the same pressure as if it alone occupied the entire vessel and the total pressure is the sum of the partial pressures of the different gases. Of course this law does not hold for gases that react with each other.

The natural consequence of this fact is that in a mixture of gases over a liquid each one dissolves according to its own partial pressure (see Henry's law as well as Dalton's) independently of the presence and pressure of other gases. For example, air is a mixture of about four volumes of nitrogen and one of oxygen. At normal pressures (760 mm.) the oxygen is responsible for only 152 mm. of this pressure and nitrogen for the other four fifths, or 608 mm. The oxygen of air dissolves in water to the exact extent that it would were the nitrogen not present. But if the nitrogen of our atmosphere suddenly ceased to exist, the oxygen remaining would exert a normal pressure of only 152 mm. and just as much of it would dissolve in rivers and lakes as at present. Oxygen at 760 mm. (five times its partial pressure in ordinary air) is five times as soluble as when found in air at 760 mm.

If a gas, not very soluble in water, is bubbled through ammonia water, for example, all the ammonia is removed because the stream of other gas (air, perhaps) sweeps the ammonia gas just above the liquid away and thus reduces its partial pressure in the air immediately above the liquid nearly to nothing at all. Since the solubility of ammonia depends in part on its pressure as a gas above the liquid, it is evident that it will, under such conditions, pass continuously out of the liquid. This is really a steady disturbance of solution equilibrium. Air and steam are both used to remove volatile substances from solution. In boiling ammonia water the escape of steam bubbles does much the same thing as if a stream of steam were led into the solution from outside.

EXERCISE 9.—How could you increase the solubility of carbon dioxide in water? How decrease it? Explain the effervescence of soda water.

Distribution Law.—In the chapter on the halogens some mention was made of the very slight solubility of iodine in water and its great solubility in carbon disulfide. A dilute solution of iodine in carbon disulfide has a beautiful violet color. At greater concentrations the solution is almost black. If we shake a small crystal of iodine in water until saturated, filter and then add carbon disulfide to the filtrate, with shaking, we observe a violet color in the heavy carbon disulfide layer. Most of the iodine has been *extracted* from the aqueous solution by the carbon disulfide, in which it is far more soluble. In fact the iodine is divided between the two solvents (if equal volumes are used) in the exact ratio of its solubility in the two. If it is one hundred times as soluble in carbon disulfide as in water, only one part will remain in the water and one hundred parts in the carbon disulfide. The dissolved iodine is in constant motion, passing from one liquid to the other, as indicated by the following equilibrium:

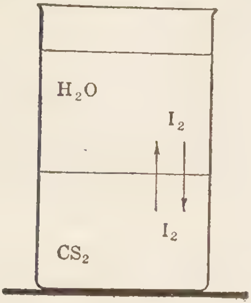

FIG. 51.—Distribution.

$$I_2 \text{ (in water)} \rightleftarrows I_2 \text{ (in carbon disulfide)}.$$

This equilibrium can be disturbed by adding something that reacts with the iodine in the water layer. Sodium thiosulfate ("hypo") or even sodium hydroxide will do this. As fast as the very small amount of iodine left in the water is used up, more replaces it from the carbon disulfide and finally, after sufficient additions with shaking, all the iodine is removed from the carbon disulfide, as shown by the complete loss of violet color.

EXERCISE 10.—What is the reaction between chlorine water and iodine? Delay this answer until the halogens have been studied.

Molar and Normal Solutions.—*A molar solution contains a molecular weight in grams (one mol) of solute in a liter of solution.* Since the molecular weight of sulfuric acid is 98, a molar solution of this acid contains 98 g. per liter. Note that we did not refer to 1000 cc. of solvent, but to 1000 cc. of solution, a very different thing. A molar solution of sodium chloride contains 58.46 g. per liter of solution.

EXERCISE 11.—How could you make 500 cc. of molar copper sulfate? Remember that the "blue vitriol" used is $CuSO_4 \cdot 5\,H_2O$.

EXERCISE 12.—How could you make half-molar potassium nitrate?

A normal solution of an acid, base, or salt contains one gram-equivalent weight of the solute in one liter of solution. The equivalent weight of hydrogen is 1.008, of oxygen 8, of sodium 23, but these are elements. Now the following equation shows that 36.468 g. of hydrogen chloride (in water solution) are equivalent to 23 g. of sodium.

$$\begin{array}{ccccccc} \mathrm{Na} & + & \mathrm{HCl} & \longrightarrow & \mathrm{H} & + & \mathrm{NaCl.} \\ 23\text{ g.} & & 36.468\text{ g.} & & 1.008\text{ g.} & & 58.46\text{ g.} \end{array}$$

Since 23 has already been determined (page 10) as the equivalent weight of sodium, it is now in order to write 36.468 as the equivalent weight of hydrogen chloride. In fact, the equivalent weight of a compound is that weight of it which reacts exactly with one equivalent weight of any element.

$$\begin{array}{ccccccc} 2\ \mathrm{Na} & + & \mathrm{H_2SO_4} & \longrightarrow & 2\ \mathrm{H} & + & \mathrm{Na_2SO_4.} \\ 46\text{ g.} & & 98\text{ g.} & & 2.016\text{ g.} & & 142.07\text{ g.} \end{array}$$

From the above equations it is seen that one mol of HCl is equivalent to 23 g. of sodium, and that one mol of H_2SO_4 is equivalent to 46 g. of sodium. So to make a normal solution of hydrogen chloride we need dissolve only one formula weight (36.468) in one liter of solution, but in the case of H_2SO_4 the entire formula weight (98 g.) is too much—we use only half the formula weight in a liter of solution, because of those two replaceable hydrogen atoms in the H_2SO_4 molecule. Of H_3PO_4 we use one third the formula weight. Apparently ***a normal solution of an acid contains 1.008 g. of replaceable hydrogen in one liter of solution. A normal solution of a base must, consequently, contain 17.008 g. of hydroxyl (−OH groups) per liter of solution*** as shown by the following equation:

$$\begin{array}{ccccccc} \mathrm{Na}\,\boxed{\mathrm{OH} \quad + \quad \mathrm{H}}\,\mathrm{Cl} & \longrightarrow & \mathrm{H_2O} & + & \mathrm{NaCl.} \\ 40.008\text{ g.} \qquad 36.468\text{ g.} & & 18.016\text{ g.} & & 58.46\text{ g.} \end{array}$$

In the case of NaOH this would require a total weight of 40.008 g. of this base in order to secure the 17.008 g. of hydroxyl. (One mol and one formula weight are the same.)

The symbol for normal is N. Twice normal is 2 N and tenth normal 0.1 N or N/10.

An Equivalent Weight of any salt is, in general, the weight containing one equivalent weight of the metal. Obviously a normal solution of copper sulphate must contain in one liter an equivalent weight of combined copper ($\frac{1}{2}$ of 63.57 g.). In actual practice $CuSO_4 \cdot 5\ H_2O$ would be weighed so the molecular weight should include the water of crystallization. One gram-mol (gram-molecular weight) of $AlCl_3$ obviously contains 27 grams of the metal yet 9 is the equivalent weight of aluminum. Hence the molar weight contains three times the equivalent weight of the metal. The equivalent weight of $AlCl_3$ is obtained by dividing the molecular weight in grams by three, the valence of the metal.

To sum up the equivalence of elements, acids, bases, and salts the following paragraph is offered:

23 g. Na = 1.008 g. hydrogen = 8 g. oxygen
36.468 g. HCl = 23 g. Na = 8 g. oxygen
49.0 g. H_2SO_4 = 23 g. Na = 8 g. oxygen
40.008 g. NaOH = 36.468 g. HCl = 8 g. oxygen
58.46 g. NaCl = 23 g. Na = 8 g. oxygen
79.82 g. $CuSO_4$ = 31.785 g. Cu = 8 g. oxygen

Exercise 13.—How could you make a normal solution of hydrobromic acid (HBr)? Of potassium hydroxide? Of barium hydroxide, $Ba(OH)_2$?

Exercise 14.—How many grams of $Na_2SO_4 \cdot 10\,H_2O$ in 800 cc. of N/5 solution? Of Na_2SO_4 in 800 cc. of N/5 solution?

Exercise 15.—Define equivalent weights.

Exercise 16.—Review the topics referring to vapor tension, deliquescence, and equilibrium. Now predict what must happen under the conditions represented in Fig. 54. Under the bell jar are two beakers; one containing a water solution (of sugar, for example) and the other pure water.

Freezing Point Lowering.—That salt water freezes at a lower temperature than pure water has long been known. Cavendish's secretary, Blagden, observed that the amount of this lowering of the freezing point is proportional to the concentrations of dissolved substance. For example, if a solution of 10 g. of glycerine in 1000 g. of water freezes a fraction of a degree below zero, then 20 g. of glycerine per 1000 g. of water must freeze twice as far below zero and a 50 g. solution five times as far below zero. A most interesting point is brought out if gram-molecular weights of such substances as alcohol, glycerine, sugar, and acetone, in 1000 g. of water are frozen. They all freeze at about $-1.86°$. Hence ***the molar depression of the freezing point of water is 1.86°.*** We can obtain the molecular weight of a soluble substance by noting how many grams of it must be dissolved in 1000 g. of water to lower the freezing point to $-1.86°$. If 80 g. are required, 80 is, of course, the molecular weight. If in another instance a solution freezes at −0.186°, the lowering is only one tenth that produced by a molar weight, and hence the weight of solute used per 1000 g. of water is only one tenth the molecular weight.

A solution of 46 g. of ethyl alcohol (C_2H_5OH) in 1000 g. of water freezes at −1.86°, as does 342 g. of cane sugar ($C_{12}H_{22}O_{11}$) and 32 g. of methyl alcohol (CH_3OH). These are all gram-molecular weights. An important exception to these statements must be made for acids, bases, and salts. They will be discussed later.

Common salt and ice in right proportions make a freezing mixture used in ordinary ice-cream freezers because the salt lowers the freezing point of water to −21° C. Calcium chloride, which, being more soluble lowers the freezing point water still more, is being used to melt the snow on city streets.

Exercise 17.—If a solution made by dissolving 8 g. of a substance in 1000 g. of water freezes at − 0.4°, what is the molecular weight of the substance?

The molecular depression of the freezing point of benzene is 5.12° and of phenol 7.27°. Of course we refer this to 1000 g. of solvent as, indeed, is also true for water.

Exercise 18.—How much should 6.5 g. of naphthalene ($C_{10}H_8$) in 125 g. of benzene lower the freezing point?

In calculating the molecular weight of a substance soluble in water the following proportion will be found useful.

Observed lowering : 1.86 = Grams of solute in 1000 g. solvent : mol. weight of solute.

Low Freezing Solutions.—Automobile radiators are filled, in winter, with water solutions of sufficiently low freezing point to keep the water fluid. Calcium chloride is cheap, very soluble, and can lower the freezing point of water very considerably. Unfortunately this and all other salt solutions are corrosive and cause damage to the engine jacket or radiator. Alcohol and the better grades of glycerine are suitable additions to water, but ethylene glycol (sold under a trade name) is the best. The Bureau of Standards table given below is a guide to the car owner. The freezing points are given on the Fahrenheit scale and should be calculated also on the Centigrade scale.

Example: If denatured alcohol is used, minimum temperature is 20 degrees and the radiator holds 3½ gallons, the radiator solution must contain 19 per cent alcohol, that is, about one fifth of it by volume.

Frozen dynamite (nitroglycerine plus fine wood meal, nitrates, etc.) sometimes explodes on rapid thawing, hence the necessity of lowering the freezing

NON-FREEZE MIXTURES FOR AUTOMOBILE RADIATORS

PERCENTAGE, BY VOLUME, IN WATER

Freezing Temperature F.	Denatured Alcohol	Wood Alcohol	Distilled Glycerine	Ethylene Glycol
20°	19	12	22	16
10°	30	20	32	25
0°	38	29	40	32
−10°	45	34	47	39
−20°	52	40	54	44

point of nitroglycerine (12.3° C.) by addition of dinitrotoluene or ethylene glycol dinitrate.

A cheap ***cooling solution*** for laboratory experiments is prepared by quickly stirring together 100 g. NH_4Cl, 300 g. H_2O, and 150 g. $Na_2CO_3.10H_2O$. The temperature falls to $-31°$ C. and the wet beaker freezes to a block of wood.

Winter Hardiness of Plants.—The winter hardiness of wheat and other plants grown in cold northern climates is closely related to the freezing point of the water solutions or plant sap. In fact this ability to stand low temperatures can be predicted by laboratory measurements of the freezing points of the plant sap, a useful method, multiplying greatly the resources of tedious field testing. Part of the water is not free but "bound" by the plant tissues. The term "bound" may be better understood after a study of the chapter on colloid chemistry. Bound water does not freeze at zero.

"Why do the leaves of evergreens hang on all winter long, when by rights they should be frozen and drop off?" According to F. W. Gail they stick because in winter their sap becomes too thick to freeze.

This investigator gathered leaves from pine trees and from broad-leaved evergreen shrubs once every month through three years, crushed out the sap and tested it for its freezing point. He found that during the summer when the weather is warm and the sap flows freely it is relatively thin and could be frozen easily if there were any frost to freeze it. But as fall comes the starch in the leaves is converted into sugars and oil, changing the sap from a thin and watery fluid into a sort of sirupy emulsion, very difficult to freeze. He found that the greatest density of the sap was reached during late January and February, when the most severe freezing weather occurs. Deciduous trees, that lose their leaves in autumn, show some thickening up of the sap, but apparently the sugars are transferred into the tree before the leaves drop off, for it was found that the sap pressed from leaves that had just fallen was easily frozen, whereas sap from leaves not quite ready to fall resisted the effects of considerably lower temperatures. (*Science Service.*)

Boiling Point Rise and Vapor Pressure.—The work of Raoult on freezing point lowering was applied (1882) to a study of the effect of dissolved substances on vapor pressure. A non-volatile solute interferes with the evaporation of a solvent by getting in the way of escaping molecules, thus lowering the vapor pressure of the solvent. Consequently the solution must be made hotter to produce a vapor pressure just equal to the pressure of the atmosphere, that is, to make the liquid boil at 760 mm. Water boils at 100°, but Raoult found that if a molecular weight in grams of any comparatively non-volatile substance (except acids, bases, and salts) is dissolved in 1000 cc. of water, the solution boils at 100.52°. The boiling point rise is 0.52°. Obviously the molecular weight of such a substance as glycerine or sugar may be obtained by measuring the boiling point of any convenient solution and from this calculating how many grams of solute would be required to raise the boiling point 0.52°. To sum it up, the lowering of the vapor pressure of a solvent (and the consequent rise in boiling point) caused by dissolved substances other than acids, bases, and salts, is directly proportional to the molecular concentration of the solute. ***The boiling point rise caused by one formula weight in grams of solute per 1000 grams of solvent is 0.52° for water,*** 1.67° for acetone, and 2.67° for benzene. Raoult's law does not hold where there is reaction between solute and solvent.

Exercise 19.—What should be the boiling point of a solution containing 150 g. of cane sugar ($C_{12}H_{22}O_{11}$) in 800 cc. of water?

Exercise 20.—A solution of 45 g. of AB in 1000 g. of benzene freezes at − 1.2°. Benzene freezes at 5.4°.—What is the molecular weight of AB?

A static method of measuring the vapor pressure of solutions has been developed, at Johns Hopkins University, with such accuracy that the vapor pressure difference between solvent and solution is determined with an error of less than 0.001 mm. mercury.

There are some very soluble substances of low aqueous tension, such as calcium chloride, which become wet in ordinary air. Such substances are ***deliquescent.*** They dissolve in the film of moisture on their surface, forming a concentrated solution of lower vapor tension than the air. Consequently moisture is deposited in the solution, tending to dilute it. This explains the use of anhydrous calcium chloride as a drying agent to take up moisture from gases. The mere fact that the aqueous tension of ordinary air may be greater than that of some crystals is not enough to account for deliquescence, otherwise water from the air would continue to condense on powdered diamonds or sand.

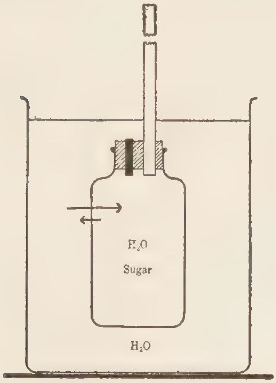

FIG. 52.—Osmotic pressure tube.

Some anhydrous substances also readily take up moisture to form hydrates of even lower vapor tension than their saturated solutions. Anhydrous barium perchlorate acts as an excellent drying agent by taking up just enough water vapor to form the trihydrate, $Ba(ClO_4)_2 \cdot 3\ H_2O$.

Osmotic Pressure.—The walls of plant cells, the membrane lining an egg shell, bladder tissue, parchment paper, and many other membranes are semi-permeable. They permit the diffusion of water while checking or prohibiting the passage of certain dissolved substances. Osmosis is the term applied to this selective flow of one or more components of a solution and the resulting pressure set up is called osmotic pressure.

In Fig. 52 we represent a simple device for demonstrating osmotic pressure which is, however, too crude for accurate quantitative study. A "thimble" of wet parchment paper is tied over the end of a thistle tube and the tube partly filled with a concentrated sugar solution containing a little coloring material, such as cochineal. The tube is firmly fixed in an inverted position in a beaker of pure water. After a few hours the level of the liquid in the narrow stem (marked with a label) has risen to a considerable height—to such a height that the weight of the column of liquid just equals the osmotic pressure of the solution. If a narrow-stemmed funnel is not at hand, a coarse capillary tube can be connected to the cup of the thistle-tube. The rate of entrance of liquid into the bulb is thus magnified to the eye. Osmotic pressure is also observed when two solutions of different concentrations are separated by a suitable membrane permeable to the solvent but not to the solute.

The pure water passes through the membrane (slowly) in both directions, but passes into the solution faster than it passes out.

The result is an increase in the volume of liquid in the bulb shown by a rise in the narrow tube. The pressure set up is measured by the weight of the column of solution.

According to the molecular theory molecules of water are in rapid motion in all directions. Since the dissolved sugar molecules get in the way of the water molecules it is evident that a square centimeter of membrane will be hit by more water molecules per second on the pure water side than on the solution side. Another method of measurement is to note the exact amount of pressure applied to the solution that just prevents dilution of the solution.

A parallel experiment with gases helps to make clear our conceptions of osmotic pressure. A large thistle tube (or its equivalent) is bent as in Fig. 53 and after filling the bend with some oil (water will not do and mercury is too heavy to show the pressure clearly) the top is tightly closed with thin linen thoroughly wet with water. This film of water is a membrane permeable to ammonia gas but only slightly permeable to air. A large beaker filled with ammonia gas is inverted over the thistle tube, and, if necessary, a stream of the gas led into the beaker from a generator. Ammonia dissolves in the film of water and escapes into the air space within the bulb. A bit of wet red litmus paper in the bulb turns blue. Since the air does not dissolve noticeably in the water, the flow of gas is all one way except that the ammonia on reaching the interior of the bulb naturally diffuses out. Soon the pressure of ammonia on both sides of the membrane will be the same, in this experiment one atmosphere. But the air within the bulb was put there under one atmosphere so the total pressure within the bulb becomes two atmospheres—one due to air and one to ammonia. This pressure is shown by rise of oil in the outer arm of the bent tube or manometer. When equilibrium is reached the pressure on the wet-linen membrane is actually due to the pressure exerted by the air within the bulb. In actual practice the weak water film breaks and the full theoretical pressure is not attained.

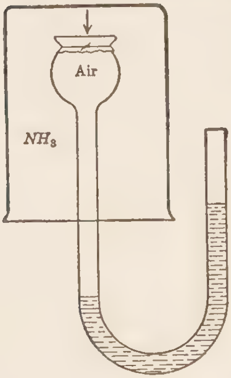

FIG. 53.—Osmotic pressure with a water film as membrane.

This latter experiment may be compared with the one using sugar solutions and water on opposite sides of a parchment-paper membrane. In the second case water on both sides moves freely through and comes to equilibrium when the pressure due to water alone is the same on both sides. The additional pressure on the membrane due to sugar molecules is what we measure as osmotic pressure. However, we measure directly the pressure with which water tends to flow in. In the first case the air inclosed in the bulb is comparable to the sugar and the ammonia present on both sides of the water film after equilibrium is comparable to the water in the other experiment. There are different theories as to the cause of osmotic pressure, but the above is a very good working conception of the phenomenon. As to the facts of osmotic pressure there is general agreement.

Using solutions against solvent we find the ***osmotic pressure is proportional to the concentration of the solute in the solution.*** That is, a 10 per cent sugar solution has twice the osmotic pressure of a 5 per cent solution. If a more dilute solution is placed on one side and a more concentrated on the other, the pressure will be proportional to the difference in concentration. Water (or other solvent) always tends to dilute the solution of greater concentration. This tendency can be checked, as was mentioned before, by applying an equal and opposite pressure.

The osmotic pressure is directly proportional to the absolute temperature. This is really Charles' law for gases. Another fact of importance is that ***at the same temperature equal numbers of molecules of different solutes in equal volumes of the solvent exert the same osmotic pressures.*** It makes no difference whether large sugar molecules (342) or molecules one tenth their weight are compared. Mere ***number of dissolved particles*** per 1000 g. solvent is all that counts. Furthermore, ***the osmotic pressure of a dissolved substance is equal to the pressure it would exert if it were a gas occupying the same volume as that of the solvent.*** Suppose that a gas of molecular weight 64 were quite soluble in water. This weight in grams (64 g.) occupying 22.4 liters (the G. M. V.) at 0° exerts one atmosphere pressure as a gas. If the same 64 g. of the gas is dissolved in 22.4 liters of water, its osmotic pressure equals one atmosphere and if dissolved in only 1 liter of water its osmotic pressure would be 22.4 atmospheres because this solution, is 22.4 times as concentrated as the other. This is similar to Boyle's law for gases.

The excess pressure which must be applied to a solution, as compared with the pure solvent, to produce a state of equilibrium so that the solvent flows at equal rates in both directions through a semipermeable membrane defines the osmotic pressure of the solution experimentally.

The semi-permeable membranes cannot be mere molecular sieves because when a pig's bladder filled with a mixture of methyl alcohol and ether was suspended in alcohol only alcohol diffused through the membrane while a rubber sack filled with the same solution permitted only the ether to pass through. It is well known that ether is soluble in rubber, while alcohol is not. This experiment parallels somewhat the experience with air-ammonia separated from air by a water membrane in which only the ammonia dissolves.

NOTE: A parchment paper cup softened by soaking in water may be attached to a rubber stopper through which passes a long tube about 2 mm. in diameter, in order to demonstrate osmotic pressure. A simple osmometer may also be set up with a collodion sac connected as in Figure 52. After the fresh wet sac is firmly attached to the No. 4 or 5 two-holed rubber stopper it is filled with a sugar solution through a thistle tube until the liquid runs out the second hole in the stopper. This hole is then closed with a glass plug, the thistle tube disconnected at A and replaced by a long section of glass tubing of about 2 mm. bore. The apparatus is next supported so that the sac is immersed in water. To prepare the sac, pour a few cc. of alcohol-ether solution of cellulose nitrate ("collodion") into a dry 100 cc. wide-mouth bottle and rotate and tilt the bottle to secure a uniform film. As the ether evaporates the film becomes sticky. Blow out the ether vapors occasionally, and after the ether odor is all gone, rinse out the alcohol (soluble in water) with water. Gently loosen the film of cellulose nitrate at the top and pour water between it and the glass. It will then be easy to remove the sac without tearing it. These collodion sacs must be kept wet or they shrivel and become far less permeable.

A spectacular experiment illustrating osmotic pressure as well as the formation of semipermeable membranes is easily performed. Crystals of salts of nickel, cobalt, copper, lead, manganese, and small lumps of ferric chloride may be dropped into ordinary commercial water glass (sodium silicate) diluted with two or three volumes of water. The fragment of nickel sulfate, for example, dissolving in the water of this solution reacts to form nickel silicate, a gelatinous material. This forms a sack, semipermeable in that it allows water to pass through in both directions but does not permit the molecules of nickel sulfate inside the sack to diffuse out. The concentration of the solution inside each little sack is greater than that outside because the fragment of crystal keeps it saturated. The result is shown by swelling and bursting of the sack. This lets out the contents, nickel sulfate, to react and form a new sack wall. Thus a tree-like growth upward (because of the lesser hydrostatic pressure above) appears with a startling rapidity in the case of ferric chloride and is quite appreciable in all cases. The "submarine forest" in many colors is worth observing for a day or so. The bursting of the sacks is a result of osmotic pressure of a more concentrated solution.

The most accurate measurements of osmotic pressure were made by Morse, Frazer, and Holland at the Johns Hopkins University and by the Earl of Berkeley in England. Morse, in his classic research, used copper ferrocyanide supported by a clay wall as the membrane. Finely ground and sifted clays were pressed wet into a solid mass which was drilled into the form of a cup and then baked. This was filled with copper sulfate solution and set in a larger vessel of potassium ferrocyanide solution. The two solutions, aided in diffusion by an electric current, met inside the wall and formed a red precipitate of copper ferrocyanide. A mercury manometer was carefully attached to the cleaned cell or cup which had been filled with the solution whose osmotic pressure was to be measured. The cell was then placed in pure water in a bath whose temperature was carefully regulated. After equilibrium was reached the pressure was read. Many difficult precautions had to be taken, but pressures of many atmospheres were accurately measured. Frazer and Myrick (1916) used delicate electric resistance methods of measuring very high pressures and reported accurate measurements of 270 atmospheres.

The osmotic pressure laws do not hold for acids, bases, and salts for very good reasons soon to be developed.

The most recent explanation of the rise of sap in plants is not based on osmotic pressure but upon the fact that a continuous column of water in a sealed vessel has a strength like a woven rope, resisting a breaking strain of several hundreds of pounds per square inch. This tensile strength of water is sufficient to pull sap up to the tops of the tallest trees as though each microscopic water tube in the sapwood had a slender steel wire strung through it. The evaporation at the leaf surfaces furnishes the pull, and the water-columns themselves act as cords to lift themselves.

Kinetic Molecular View of Osmotic Pressure.—Van't Hoff concluded that *substances in solution behave as if they were gases confined to the volume of the pure solvent.* Thus osmotic pressure is really quite similar to gas pressure and the laws of Boyle and

Charles hold both for gases and for solutions (with certain exceptions).

Surface Tension of Solutions.—The surface tension of water (p. 62) is relatively high, equivalent to a force of 72.8 dynes, but substances such as the common soaps, proteins in the presence of acid or base, saponins, bile salts, etc., lower this value considerably. The surface tension of water is lowered to 31 dynes in extremely dilute solutions of sodium oleate (a soap of the pure "castile" type). Any substance that lowers surface tension concentrates at the surface, forming a film.

Salts in true solution generally raise the surface tension of water and so do the opposite from the film formers—they draw away from the surface. Harkins shows that on the surface of a dilute water solution of sodium chloride there is an extremely thin layer of pure water about 0.000,000,04 cm. thick. The film becomes thinner as the concentration of the original salt solution increases.

Liquid Ammonia Solution.—Although liquefied ammonia gas (NH_3) is obtained and kept only by moderate cooling and compressing and hence is inconvenient for ordinary laboratory work, it is, none the less, an interesting solvent. Many salts, bases, and other compounds dissolve in it, but the comparative solubilities are often surprising. Silver chloride is insoluble. Sodium chloride is soluble, and potassium chloride insoluble. Sodium, potassium, calcium, and the active metals of their class dissolve readily and are recovered as beautiful crystals when the ammonia is carefully evaporated. At − 33° C. it is possible to dissolve 49 g. of metallic potassium in 100 g. of liquefied ammonia. On evaporation of the solvent from ammonia solutions of certain salts the salts separate with "ammonia of crystallization," quite analagous to the formation of hydrates in water solution. Would the term "ammonia of solvation" apply in this instance?

EXERCISES

21. Alcohol, C_2H_6O, is both volatile and water-soluble. What is the osmotic pressure (in atmospheres) of a solution made by dissolving 6 g. of alcohol in one liter of water?

22. State Henry's law and give an illustration.

23. State the law of partial pressures. If you have ammonia gas at a pressure of 100 mm. in a closed bottle half filled with water, would the weight dissolved be changed by the introduction of nitrogen at an additional pressure of 200 mm.?

24. What do you mean by a gram-equivalent weight of hydrogen? Of sodium? Of magnesium? Of copper? Of aluminum? Of sodium chloride? Of sodium sulfate? Of sulfuric acid? Of aluminum sulfate? Of sodium hydroxide? Of barium hydroxide ($Ba(OH)_2$)?

25. Why does a lump of anhydrous calcium chloride deliquesce in ordinary air while a diamond does not?

26. If you filled a bladder (semipermeable membrane) with a 0.2 M. solution of sugar in water and placed it in a 0.1 M. sugar solution, what would happen?

27. Prove that a solution is a mixture rather than a compound.

28. What weights of (1) alcohol, C_2H_6O, (2) glycerol, $C_3H_8O_3$, (3) ethylene glycol ("Prestone"), $C_2H_6O_2$, would be necessary to lower the freezing point of 24 liters of water 12°?

29. What weights of the following substances would be required to prepare one liter of normal solution; HCl, $NaOH$, H_3PO_4, Na_2SO_4, $Na_2SO_4 \cdot 10\,H_2O$, $BaCl_2 \cdot 2H_2O$, $AlCl_3$?

30. Calculate the volume of 1 M. sulfuric acid required for reaction with each of the following: 28 g. calcium oxide; 13 g. magnesium oxide; 12.4 g. of aluminum oxide.

31. If 26 g. of a substance dissolved in 500 g. of water gives a solution boiling at 100.26°, what is the molecular weight of the substance?

32. If 68.5 g. of a substance dissolved in 500 g. of water gives a solution freezing at − 1.86°, what is the molecular weight of the substance?

No. of Gram
MW

Mole x MW
g

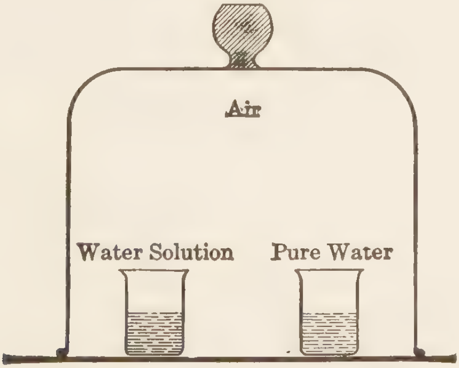

FIG. 54.—What will happen under this bell-jar?

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CHAPTER XII

CHLORINE, BROMINE, IODINE, AND FLUORINE

	At. Wt.	Melting Pt.	Boiling Pt.	Color and State
Fluorine (F)	19.00	−223°	−187.0°	Pale-yellow gas
Chlorine (Cl)	35.46	−102°	−33.6°	Greenish-yellow gas
Bromine (Br)	79.92	−7°	63.0°	Reddish-brown liquid
Iodine (I)	126.92	113°	184.4°	Violet-black solid

The Halogen Family.—Chlorine, bromine, iodine, and fluorine exhibit such close resemblances as elements and in their compounds that they are grouped as a family of "halogens." Of all the elements they are the least like the metals. The name *halogen* means "salt former," given because they all unite with metals to form salts, such as sodium chloride.

Chlorine

History.—Chlorine was first prepared by Scheele in 1774 by the action of manganese dioxide on hydrochloric acid. However, it was thought to be a compound of hydrochloric acid and oxygen, even by Lavoisier. In 1810 Sir Humphry Davy tried in vain to reduce the supposed oxide and finally convinced the scientific world that this substance was really an element. He named it chlorine, from the Greek for "greenish-yellow."

Exercise 1.—In what connection have we heard of Scheele before?

Occurrence.—Chlorine is not found free in nature because it reacts so readily with many other substances, particularly metals. Its commonest compound is sodium chloride, common salt. This is found in sea water to the extent of nearly 3 per cent. Great Salt Lake contains 23 per cent. In some parts of the world salt is mined, and deposits are common. Magnesium chloride generally occurs with common salt. In fact the "wetting" of table salt and consequent refusal to go through the top of shakers is due largely to the deliquescence of the magnesium chloride impurity. Potassium chloride is found in a large deposit at Stassfurt, Germany, associated with sodium chloride and magnesium chloride. Silver chloride, "horn silver," is one of the ores of silver.

Preparation.—The most convenient laboratory methods of preparation depend upon the oxidation of hydrogen chloride into water and free chlorine:

$$\boxed{O + 2\,H}Cl \longrightarrow H_2O + Cl_2.$$

Oxygen alone does this only with extreme slowness unless aided by a catalyst at a favorable temperature, but good oxidizing agents such as potassium permanganate, manganese dioxide, sodium dichromate, and lead dioxide will oxidize it rapidly without a catalyst. A concentrated solution of hydrogen chloride in water (called hydrochloric acid) is warmed (Fig. 55) with the oxidizing agent:

$$MnO_2 + 4\,HCl \longrightarrow 2\,H_2O + MnCl_4,$$
$$MnCl_4 \longrightarrow MnCl_2 + Cl_2.$$

The manganese tetrachloride, $MnCl_4$, is an oily liquid, unstable unless kept chilled. Consequently it breaks down at room temperatures into the ordinary manganous chloride and free chlorine. Had we used manganous oxide, MnO, no chlorine would have been released:

$$MnO + 2\,HCl \longrightarrow H_2O + MnCl_2.$$

We may say that MnO_2 is an oxidizing agent and MnO is not, but this is only part of the truth. In MnO_2 the valence of the metal is four, and in its product, $MnCl_2$, the valence has dropped to two. This fact introduced an extension of the idea of *oxidation* and *reduction*. A drop in valence of the positive element or radical in a compound is reduction. The MnO_2 was *reduced* by the HCl (which also means that the MnO_2 oxidized the HCl) because the manganese dropped in valence from four to two. In the reaction with MnO the valence of manganese was two and remained two in the product, $MnCl_2$.

Exercise 2.—The reactions of hydrochloric acid with lead dioxide, PbO_2, and lead monoxide, PbO, are similar to the above. Write the equations. Remember that the hydrogen of the acid unites with the oxygen of metallic oxides to form water.

In practice we generate the hydrochloric acid from the action of moderately diluted sulfuric acid on sodium chloride and oxidize it with manganese dioxide in the same operation (Fig. 55). The gas is passed through a little water to remove hydrogen chloride and through concentrated sulfuric acid to dry it. It displaces air from the receiving cylinder.

$$\begin{array}{ll} (1) & 2\,NaCl + 2\,H_2SO_4 \longrightarrow 2\,NaHSO_4 + \cancel{2\,HCl} \\ (2) & \cancel{4\,HCl} + MnO_2 \longrightarrow 2\,H_2O + \cancel{MnCl_2} + Cl_2 \\ (3) & \cancel{MnCl_2} + H_2SO_4 \longrightarrow MnSO + \cancel{2\,HCl} \\ \hline (4) & 2NaCl + 3H_2SO_4 + MnO_2 \longrightarrow 2NaHSO_4 + 2H_2O + MnSO_4 + Cl_2. \end{array}$$

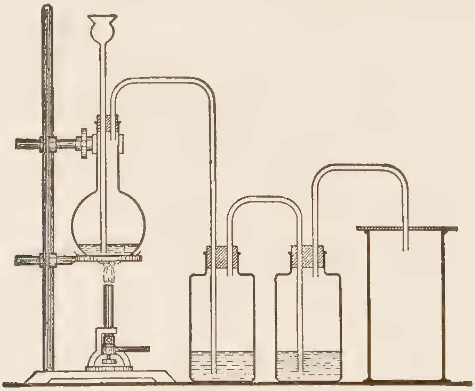

FIG. 55.—Preparation of chlorine.

Equations (1), (2), and (3) represent the *steps* in the complete reaction summed up in (4). In attempting to add (1), (2), and (3) to get (4) we must write on the left all the reacting substances originally mixed and on the right the final products. The intermediate substances are not included in a summary (HCl and $MnCl_2$ in this instance). Such a summary is difficult to remember and it is not best to attempt it. It may be worked out at any time by a logical development of the easily remembered steps.

Potassium permanganate is an excellent but expensive oxidizing agent for the purpose of making chlorine. Concentrated hydrochloric acid diluted with about one-third its volume of water is dropped slowly on the solid from a dropping funnel. The chlorine is released instantly without warming, and its flow ceases on stopping the addition of acid:

$$2\,KMnO_4 + 16\,HCl \longrightarrow 8\,H_2O + 2\,KCl + 2\,MnCl_2 + 5\,Cl_2.$$

Potassium permanganate, being soluble in water, is in better contact with the acid than is the insoluble manganese dioxide. Sodium dichromate is also efficient in oxidizing concentrated hydrochloric acid:

$$Na_2Cr_2O_7 + 14\ HCl \longrightarrow 2\ NaCl + 2\ CrCl_3 + 7\ H_2O + 3\ Cl_2.$$

Compare this equation with the one for potassium permanganate. In each case enough hydrogen atoms from HCl molecules must be taken to unite with all the oxygen atoms of the oxidizing agent. Also, each metallic atom unites with enough chlorine atoms to form its stable chloride. Hence in the two equations the formation of KCl, $MnCl_2$, NaCl, and $CrCl_3$. Any chlorine not needed by the metals escapes as gas.

In balancing these equations representing the action of most of the oxidizing agents on HCl it is helpful to remember that the hydrogen of the HCl unites with all the oxygen of the oxidizing agent to form water while the metal (or metals as in $KMnO_4$) unite with all the chlorine they can hold (forming KCl, $MnCl_2$, etc.). The rest of the chlorine, if there is any, is liberated. Similar statements apply to HBr and HI.

✓ Exercise 3.—How many liters of chlorine are released by the action of 45 g. potassium permanganate on an equivalent amount of hydrochloric acid?

Chlorine by Electrolysis.—The leading commercial method of making chlorine, especially in the United States, is by the electrolysis of water solutions of sodium chloride. Chlorine is evolved at the anode, which must be made of carbon, usually in the form of graphite, because the gas is so active it would react with metal anodes. At the cathode, usually iron, sodium is released, but of course it reacts at once with water to form sodium hydroxide and hydrogen. The sodium hydroxide is a valuable by-product. Since chlorine in the presence of water reacts with sodium hydroxide, it is necessary to keep the solutions around the two electrodes from mixing. A single plant in West Virginia is now producing one hundred and fifty tons daily.

Molten sodium chloride conducts electricity and can thus be decomposed into chlorine and sodium. With no water present the sodium accumulates. This is one of the commercial sources of metallic sodium, but sodium hydroxide on account of its lower melting point is generally used instead of the chloride.

Physical Properties.—Chlorine is a greenish-yellow gas 2.49 times as heavy as air. One liter weighs 3.220 g. at 20°. One hundred volumes of water dissolve 226 volumes of chlorine. It can be liquefied at 18° by 16.5 atmospheres pressure and its critical temperature is 146°. The liquid boils at $-33.6°$ and freezes at $-102°$. The gas is very irritating to smell and fatal in any considerable quantities. When collected over water there is some loss because it dissolves in and reacts with water. It is less soluble, however, in water saturated with common salt. Since it attacks mercury it may not be collected over that liquid. Usually it is led into the bottom of any vessel filled with air and, being 2.49 times as heavy, displaces the air upward. Water saturated with chlorine at 0° deposits crystals of $Cl_2 \cdot 8\ H_2O$. These have a very high vapor tension, decomposing readily on warming slightly. Faraday in 1823 used this property to liquefy chlorine, the first time this was achieved. Now every gas has been liquefied.

Faraday sealed some crystals of the chlorine hydrate in a strong U-tube, warmed the end containing the crystals, and chilled the other end by ice and salt (Fig. 56). In the closed tube the pressure of the liberated chlorine became great enough with the aid of low temperature to liquefy the gas. The molecules were forced together by pressure and their motion lessened by cooling.

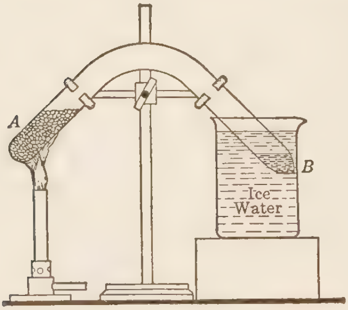

Fig. 56.—Liquefaction of chlorine by pressure and cooling.

Chlorine, under pressure, is now shipped in tank cars containing 15 tons of the liquid element.

Chemical Properties.—Chlorine is one of the most active elements, more active than oxygen. It unites with nearly all the elements to form ***chlorides.***

1. Action on Elements. The metals, with but few exceptions, unite with chlorine. A piece of sodium in a bottle of *dry* chlorine gradually becomes sodium chloride, but if the sodium is first heated it burns brilliantly in the chlorine. So does calcium, forming calcium chloride. Thin copper foil, if heated, bursts into flame in a jar of chlorine. For a lecture-table experiment it is most convenient to evacuate a flask containing crumpled copper leaf (Dutch metal), close the stopcock, connect with a flask of chlorine (Fig. 57), and then open the stopcock. As the chlorine rushes up the *wide* tube into the upper flask a flash of flame occurs. Even platinum is attacked by the gas. Most of the non-metals are attacked. Sulfur burns in chlorine to form sulfur chloride, used in the manufacture of mustard gas during the World War.

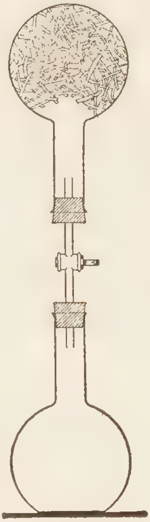

FIG. 57.—Chlorine reacting with copper foil.

Yet if chlorine is dried over phosphorus pentoxide, it does not attack copper, etc. A trace of water is necessary as a catalyst.

Phosphorus unites with chlorine, burns in it in fact, to form a colorless liquid (PCl_3), phosphorus trichloride. With an excess of chlorine this becomes PCl_5, phosphorus pentachloride, a yellow solid.

Chlorine and hydrogen unite very slowly in the dark, rapidly in diffused light, and explosively in bright sunlight or the light of burning magnesium. Hydrogen chloride is formed. If a jet of burning hydrogen is lowered into a bottle of chlorine, it continues to burn with evolution of light and heat and formation of hydrogen chloride (Fig. 58). Direct union of the two gases is being used to some extent now to form pure "synthetic hydrochloric acid." There is, therefore, such a thing as combustion without oxygen:

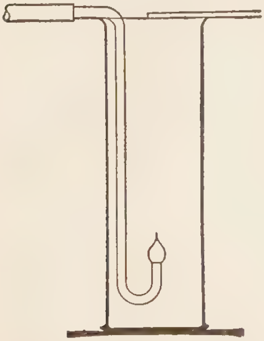

FIG. 58.—Burning methane (CH_4) in a jar of chlorine.

$$H_2 + Cl_2 \longrightarrow 2\ HCl.$$

2. *Action on Compounds.* Chlorine will pull the hydrogen out of compounds and form hydrogen chloride. Natural gas (largely CH_4, methane) will burn in chlorine just as well as does hydrogen, but the flame is smoky, due to the liberated carbon (Fig. 58).

$$CH_4 + 2\ Cl_2 \longrightarrow C + 4\ HCl.$$

A burning candle lowered into a jar of chlorine burns with a smoky flame. A paper wet with warm turpentine bursts into smoky flame in chlorine. The reaction is similar:

$$C_{10}H_{16} + 8\ Cl_2 \longrightarrow 10\ C + 16\ HCl.$$

√ Exercise 4.—How many liters of hydrogen chloride at 0° and 760 mm. can be formed by the action of chlorine on 500 g. turpentine? Solve two ways.

Chlorine displaces some elements from compounds:

$$2\ KI + Cl_2 \longrightarrow 2\ KCl + I_2,$$
$$2\ NaBr + Cl_2 \longrightarrow 2\ NaCl + Br_2.$$

Here iodine and bromine are displaced. Chlorine is a more active element than either. With carbon monoxide, catalyzed by charcoal at 100°, it unites to form phosgene, one of the greatest of poison war gases:

$$CO + Cl_2 \longrightarrow COCl_2.$$

Chlorine not only dissolves in cold water but reacts with it:

$$Cl_2 + H_2O \rightleftarrows HCl + HClO.$$

This is a reversible reaction, but the hypochlorous acid ($HClO$) slowly decomposes into hydrochloric acid and oxygen. Since this decomposition is accelerated by sunlight, chlorine water is best kept in dark bottles. Finally the equilibrium is displaced completely to the right and there is no longer any dissolved chlorine left, merely a solution of hydrochloric acid. The equilibrium is disturbed to the right rapidly if there is some reducing agent present to take up the oxygen from the hypochlorous acid. In other words the instability of hypochlorous acid makes it a good oxidizing agent.

We referred previously to the burning of a jet of methane (CH_4) in chlorine. In the sunlight the two gases react slowly as follows:

$$(1)\quad CH_4 + 3\ Cl_2 \longrightarrow CHCl_3 + 3\ HCl,$$
$$(2)\quad CH_4 + 4\ Cl_2 \longrightarrow CCl_4 + 4\ HCl.$$

$CHCl_3$ is chloroform and CCl_4 is carbon tetrachloride. This kind of displacement is sometimes called substitution. The hydrogen displaced is not set free but unites with part of the chlorine.

Types of Chemical Reaction.—

I. Combination. Two substances unite to form one substance. Example: $C + O_2 \rightarrow CO_2$.

II Decomposition. One substance decomposes into two or more. Example: $2\ HgO \rightarrow 2\ Hg + O_2$.

III. Double Decomposition. Two substances react to form two other substances. Example: $AgNO_3 + NaCl \rightarrow NaNO_3 + AgCl$.

IV. Displacement. One element displaces another from a compound. Example: $Zn + H_2SO_4 \rightarrow H_2 + ZnSO_4$.

Exercise 5.—Write three examples of each type.

Uses of Chlorine.—Chlorine finds its greatest use as a bleaching agent. Colored strips of calico, red geraniums, etc., hung in bottles of chlorine soon lose their color. If, however, the gas and the colored object are thoroughly dried, no bleaching takes place.

The effect of water is easily understood from the equation just given:

$$Cl_2 + H_2O \rightleftarrows HCl + HClO.$$

The hypochlorous acid oxidizes colored substances into colorless ones so the chlorine bleaches indirectly. Printers' ink cannot be bleached because its color is due to carbon, on which hypochlorous acid has no effect. Chlorine is too destructive to be used on silk, feathers, and the more delicate materials. Even cotton is slightly weakened, so the chlorine must be thoroughly washed out. Great quantities of the gas are passed over lime to form bleaching powder, from which chlorine can be released as needed. Chlorine finds use in the hypochlorite process of removing sulfur from gasoline.

As a disinfectant it is invaluable. Many great cities add a little chlorine to their water supplies to kill bacteria, which it does most efficiently and cheaply. Typhoid epidemics are quickly checked by its use. It has recently been shown that small amounts of chlorine are effective in allaying stenches.

Gold is extracted from its ores by the action of chlorine in forming soluble gold chloride. This is only one of the processes used.

It is possible to chlorinate the methane (CH_4) in natural gas to form chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4) but at present this is not economically successful. Many useful organic compounds are formed in similar ways. Ethylene glycol ($C_2H_4(OH)_2$), a compound quite similar to glycerine in properties and uses is derived from a chlorination product $C_2H_4Cl_2$.

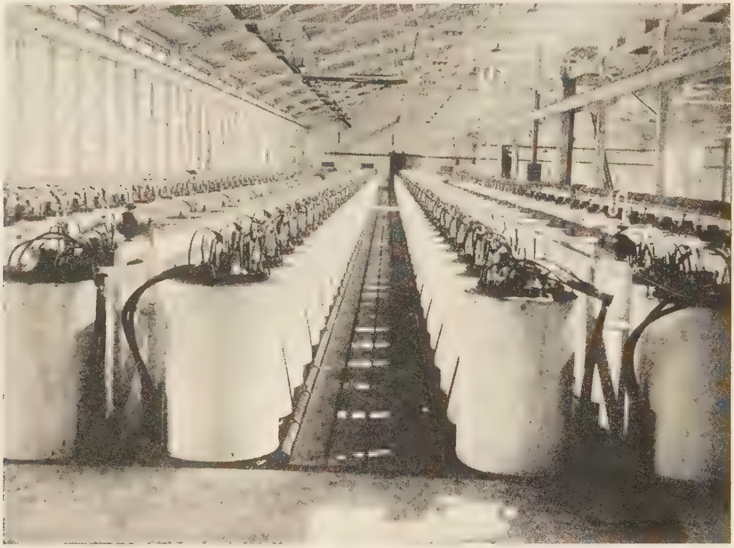

Fig. 59.—Electrolytic production of chlorine at Charleston, W. Va. (560 Vorce Cells).

Chlorine is essential to most of the poison gases used in modern warfare. Rolling clouds of chlorine were used in the earlier gas attacks. Mustard gas $(C_2H_4Cl)_2S$, phosgene, $COCl_2$, chlorpicrin (CCl_3NO_2),—these demanded huge quantities of chlorine. Mustard gas (dichlordiethylsulfide), is still the most effective toxic gas, partly because of the ease and safety of its manufacture, essentially the reaction between ethylene (C_2H_4) and sulfur monochloride (S_2Cl_2). The raw materials are easily prepared in quantity. The mustard gas penetrates the human skin and then slowly reacts with water of the body tissues with release of hydrochloric acid. This delayed hydrolysis adds greatly to its effectiveness.

An effective sternutatory, or sneeze-producer, is diphenylchlorarsine $(C_6H_5)_2$ AsCl, and the best tear gas (so useful to the police) is benzyl bromide, $C_6H_5CH_2Br$.

Marine borers in many sea harbors cause great destruction of wooden pilings. Creosoting these timbers has repelled marine borers fifteen years, but our Chemical Warfare Service has discovered toxic substances from 25 to 50 times as effective as creosote.

Two-thirds of all the chlorine produced in America is used in bleaching paper pulp, 22 per cent in bleaching textiles, 10 per cent in water purification, and 7 per cent in laundry bleaching. Until recent years chlorine was used in combination with lime as "bleaching powder." Now there is an increasing demand for liquid chlorine in steel cylinders or in tank cars. The United States now makes 30,000 tons of liquid chlorine annually.

Since dry chlorine does not attack iron, it is compressed to a liquid in heavy steel cylinders for shipment.

Tests.—Minute traces of chlorine are readily detected by smell. A filter paper soaked in a solution of potassium iodide and starch turns blue in the gas. Chlorine sets the iodine free, thus:

$$2\,KI + Cl_2 \longrightarrow 2\,KCl + I_2.$$

The *free* iodine then dissolves in the starch with development of a blue color.

BROMINE, IODINE, AND FLUORINE

The history of chlorine has already been given. Davy demonstrated its elementary nature in 1810, and very soon afterwards iodine was made by Courtois, who heated the ash of seaweed with concentrated sulfuric acid, obtaining violet vapors. This method, with some modification, is still used. Courtois did not know what he had made, but in 1814 Gay-Lussac proved that the new substance was an element and gave it the name "iodine," from the Greek for "violet."

Balard, in 1826, released bromine from a salt liquor by the action of free chlorine, the most modern method of commercial preparation we have to-day, a century later. He also treated a salt, which he later found to be potassium bromide, with concentrated sulfuric acid and manganese dioxide. Even this method is still in use.

As early as 1670 chemists knew that the mineral fluorspar (CaF_2), when warmed with concentrated sulfuric acid, produced a gas that attacked glass. Scheele suspected this mineral to be the calcium salt of some acid, but not until 1807 was the acid (H_2F_2) prepared by Gay-Lussac. All efforts to release the element fluorine from this acid failed, due to its great activity, until Moissan in 1886 isolated it by electrolyzing potassium hydrogen fluoride in solution in liquid hydrofluoric acid contained in a cooled platinum U-tube. Mathers has also prepared fluorine by electrolysis of absolutely anhydrous molten KHF_2 in a magnesium vessel using a graphite anode.

Occurrence.—The halogens are too active to occur free in nature. Sodium chloride is the most common source of chlorine.

Bromine (Br) in the form of magnesium bromide ($MgBr_2$) and sodium bromide (NaBr) is far less abundant, but it is found with the sodium chloride in sea water, in the great salt layers at Stassfurt, Germany, and in the salt brines of Michigan and West Virginia. The Unites States produces 1000 tons of bromine yearly. It occurs elsewhere, but these are the chief commercial sources. The Dead Sea contains much magnesium bromide.

The possibility of preparing bromine from sea water has been thoroughly demonstrated. When the demand and the price justify it we shall undoubtedly rely upon this exhaustless source. Quick mixing of sulfuric acid, chlorine, and aniline with sea water yields, almost instantly, crystals of tribromoaniline which can be filtered out. Although there are only 66 pounds of bromine in a million pounds of sea water a single cubic mile of this water could supply a plant producing 100,000 pounds of bromine each month for 392 years.

Iodine (I), until recent years, was obtained wholly from seaweed ash by heating with concentrated sulfuric acid and manganese dioxide. Now nearly all of it is obtained from the beds of Chili saltpeter ($NaNO_3$), where it is found to the extent of 0.2 per cent as sodium iodate ($NaIO_3$). Chili produces almost 800 tons of iodine and could easily produce ten times as much. Their monopoly leads to prices beyond reason. Recently there has been some extraction of iodine on a small scale from the giant kelp on the California coast. A small amount of an organic iodine compound, iodothyrin, is found in the thyroid gland of man. Where we are deficient in this, goiter or cretinism develops. Extracts of a sheep's thyroid gland have been administered successfully as a remedy.

McClendon has pointed out the close relation between the occurrence of goiter and the deficiency in soluble iodides in water supplies. The human body in health may contain 20 mg. of iodine, half of it being in the thyroid gland. Sea spray is blown inland to a considerable distance and may carry sufficient iodides. In certain areas the original iodides have been leached out of the soil—and goiter is prevalent. In many schools the children are given a carefully calculated amount of sodium iodide as a preventative. Some people use sodium iodide in their table salt (usually on the advice of a physician). However there is danger in the compulsory use of iodides by all adults.

An appreciable amount of iodine occurs in certain foods, especially in string beans, spinach, milk, and butter. Leafy vegetables in general and some fruits are good sources when grown on soils containing appreciable amounts of iodides. This explains why goiter is not more prevalent.

Fluorine (F) is found as fluorspar (CaF_2), cryolite (Na_3AlF_6), and apatite ($3\,Ca_3(PO_4)_2 \cdot CaF_2$). Cryolite occurs in Greenland and is of great importance in making the metal aluminum.

Preparation.—Electrolysis is the successful commercial method of preparation for chlorine. There is no commercial demand for fluorine for obvious reasons, and bromine and iodine can be made by cheaper methods. Yet some bromine is made by electrolysis.

Oxidation of hydrogen chloride has been given as one of the great methods of preparing chlorine. The preparation of fluorine by a similar method is impossible. The oxidation of hydrogen fluoride is represented by the following equation:

$$O + H_2F_2 \rightleftarrows H_2O + F_2.$$

Fluorine reacts vigorously with water to form oxygen and hydrogen fluoride; therefore the above reaction is reversed too readily to permit separation of the fluorine. Mathers' preparation of fluorine in quantity is recent.

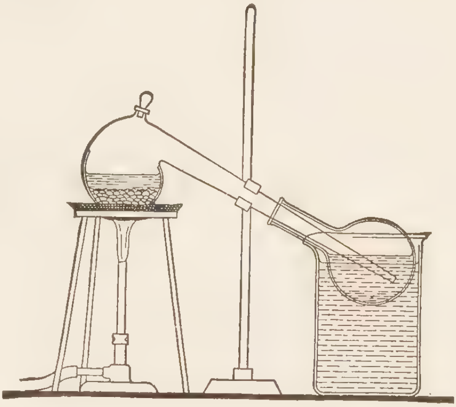

FIG. 60.—Preparation of bromine.

But oxidation serves well in the preparation of bromine and iodine. The same reaction given for chlorine applies.

A mixture of sodium bromide, manganese dioxide, and concentrated sulfuric acid is heated moderately. The vapors of bromine are condensed in a cooled flask (Fig. 60). Similar reactions are given in steps on page 160.

$$2\,NaBr + 3\,H_2SO_4 + MnO_2 \longrightarrow 2\,NaHSO_4 + MnSO_4 + 2\,H_2O + Br_2,$$
$$2\,NaI + 3\,H_2SO_4 + MnO_2 \longrightarrow 2\,NaHSO_4 + MnSO_4 + 2\,H_2O + I_2.$$

In other words, the oxidation of hydrogen bromide ($2\ HBr + O \longrightarrow H_2O + Br_2$) is a part of the mechanism of the reaction.

The brine pumped up from the salt beds underlying Midland, Michigan, and vicinity contains 0.14 of one per cent bromine (as sodium and magnesium bromides). After concentrating to crystallize out most of the salt the remaining "bitter liquor" is electrolyzed at a voltage high enough to release all the bromine but too low to discharge any chlorine. A stream of warm air carries off the bromine. Some of the bromine is cooled and condensed as a liquid, but most of it is led up through a splash tower against a "counter current" of sodium carbonate solution.

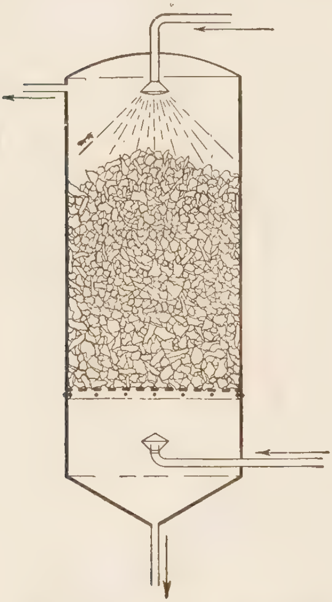

FIG. 61.—A stream of bromine gas and air meets a counter current of sodium carbonate solution.

$$(1)\quad Br_2+H_2O \rightleftarrows HBr+HBrO,$$

$$(2)\quad Na_2CO_3+HBr+HBrO \longrightarrow NaBr+NaBrO+H_2O+CO_2.$$

No bromine escapes for it meets at the top a stream of fresh sodium carbonate solution. No sodium carbonate gets through for it meets a stream of fresh bromine vapor at the bottom. Proper adjustment of the two opposing streams give efficiency. Increasing either stream after adjustment would mean a loss of bromine or of sodium carbonate as the case might be.

The mixture of NaBr and NaBrO in solution is evaporated to dryness, during which operation the NaBrO changes into $NaBrO_3$ and NaBr. It is easier and safer to ship this dry mixture to a consumer in a distant city than to ship liquid bromine. The consumer merely adds sufficient sulfuric acid to the dry salts to liberate the HBr and the $HBrO_3$. The final solid product, "mining salt," is $5\ NaBr + NaBrO$. When acidified the following reaction occurs:

$$HBrO_3 + 5\ HBr \longrightarrow 3\ H_2O + 3\ Br_2.$$

Fluorine has the greatest affinity for the metals, chlorine next, bromine third, and iodine least. So the element chlorine displaces bromine from any bromide and iodine from any iodide. Commercial use is made of this fact:

$$2\,NaBr + Cl_2 \longrightarrow 2\,NaCl + Br_2,$$
$$MgBr_2 + Cl_2 \longrightarrow MgCl_2 + Br_2.$$

Chlorine is allowed to rise through a tower down which a brine containing sodium or magnesium bromide is trickling. Iodine may be released from the sodium iodide of kelp ash in the same way.

The sodium iodate in Chili saltpeter is decomposed by sodium bisulfite:

$$2\,NaIO_3 + 5\,NaHSO_3 \longrightarrow 3\,NaHSO_4 + 2\,Na_2SO_4 + H_2O + I_2.$$

Exercise 6.—Would iodine displace bromine from a bromide?

Properties.—In addition to the table of properties at the head of this chapter it might be mentioned that we know nothing of the solubility of fluorine in water because it reacts so rapidly. At 0° chlorine dissolves in 100 cc. of water to the extent of 1.49 g., bromine 4.3 g., and iodine 0.32 g. Bromine forms a hydrate, $Br_2 \cdot 10\,H_2O$, similar to $Cl_2 \cdot 8\,H_2O$.

A most striking relation of properties to atomic weight is apparent from an examination of the table at the beginning of the chapter. The weights increase in the order fluorine, chlorine, bromine, iodine, and the melting point (freezing point) rises with increase in weight. The heaviest is a solid at room temperatures, bromine only a liquid, and the lighter ones gases. Even the depth of color increases with weight. The boiling point rises in the same order. But the activity decreases as the elements grow heavier, except towards oxygen. Fluorine refuses to unite with oxygen; the oxides of chlorine are unstable, one of them exploding below 100°; bromine has no known oxides; and even iodine pentoxide (I_2O_5) is not difficult to decompose. All the halogens unite directly with phosphorus. Iodine and white phosphorus unite vigorously with the evolution of heat, bursting into flame in fact. Several inter-halogen compounds such as ICl and IF_5 are known but none are very stable.

At ordinary temperatures these four element are diatomic, as

Cl_2, etc. But at high temperatures they dissociate into molecules made up of single atoms. At 1700° the density of iodine corresponds to a molecular weight of 127, the same as the weight of one atom. At 1043° the density of the vapor (compared to air) is 7.01, which means that only 25 per cent of the molecules have dissociated and the other 75 per cent are still I_2.

Exercise 7.—At 1275° the density of iodine vapor is 5.82 compared to air (1 liter air weighs 1.2928 g.). What percentage of the molecules have dissociated into single iodine atoms and what percentage remains as I_2? Remember Avogadro's law.

Iodine dissolves in many organic liquids, such as chloroform, carbon disulfide, hydrocarbons (in all these with violet color), alcohol, and ether (in these two with brown color). Although but slightly soluble in water, it dissolves readily in an aqueous solution of sodium or potassium iodide:

$$KI + I_2 \rightleftarrows KI_3.$$

The potassium triiodide (KI_3) is rich red and very soluble, but all efforts to separate it from solution fail. That its formation is an equilibrium reaction can be shown by testing for free iodine with starch paste (blue solution formed). By using up the little free iodine (as by adding "hypo") the equilibrium is continuously disturbed to the left and the red color fades.

A quantity of iodine in the open air volatilizes on evaporation. On heating it changes rapidly into violet vapors without passing through the liquid stage. Such a change is called *sublimation.* Iodine is sublimed to separate it from impurities.

Uses of the Halogens.—Fluorine is too difficult to make and to keep for any practical use. Ammonium fluoride is a disinfectant for brewery vessels. Sodium fluoride is an effective wood preservative and insecticide. Sodium hydrogen fluoride is much used in polishing granite. Magnesium silicofluoride ($MgSiF_6$) is soluble and finds use in hardening concrete. The mineral fluorspar, CaF_2, is essential as a flux in making open-hearth steel and is used in making white opaque glass and enamels. Melted fluorides are used as the solvent in the electrolytic manufacture of aluminum and of magnesium. Chlorine, as stated previously, is of great industrial importance.

Bromine is used in making some aniline dyes, in making potassium bromide (a valuable nerve sedative), and, in the form of silver bromide, is the sensitive material on photographic plates. Bromine was used in the World War to make "tear gases," such as bromacetone. About 1000 tons of bromine is the normal annual production in the United States. In 1924 tetraethyl lead came into extensive use as an "anti-knock" addition to gasoline. Ethylene bromide was used with this "ethyl gas" and thereby an enormously increased demand for bromine was created. About 2 cc. of $C_2H_4Br_2$ per gallon of gasoline are required to furnish enough bromine to change the lead set free in the explosion into $PbBr_2$. Free lead would injure the ignition points. There is, however, an increasing use of other anti-knock substances.

Iodine is rather expensive, finding application as silver iodide in photography, as iodides in medicine, and in the manufacture of some dyes. Iodoform (CHI_3) is a valuable antiseptic. Tincture of iodine, an alcoholic solution of the element, is of great service in medicine. As a laboratory reagent in quantitative analysis iodine is well known.

EXERCISES

8. Suppose that to-morrow a new halogen is isolated with an atomic weight of 214. Describe its properties, how the acid is made, and the properties of the acid. Call the element "Doline" (Do) and the acid hydrogen dolide or dolidic acid (HDo).

9. Make a four-column chart on which you compare the four halogens in solubility, action on water, and other properties. Compare their acids in ease of oxidation. Give tests for the four elements and the four acids.

10. From their formulas calculate the weight of one liter of hydrogen bromide and iodide and get the density in terms of air.

11. Distinguish between a chloride, bromide, and iodide (white solids as given to you) by addition of concentrated sulfuric acid.

12. Sometimes a natural salt brine containing magnesium bromide and sodium chloride is splashed down through a cylinder while a "counter current" of chlorine gas rises through the cylinder. Make a sketch of the apparatus and explain the process in detail.

13. In the manufacture of sodium peroxide aluminum trays filled with sodium are *slowly* pushed along a tube heated to 300° against a "counter current" of dry air. Remembering that the reaction between sodium and oxygen is rather violent at 300°, will you explain (with a drawing) the advantages of the counter-current principle as applied in this case?

14. A kilogram of sodium bromide is treated with sulfuric acid and manganese dioxide. (a) What weight of bromine is liberated? (b) What weights

of sulfuric acid and manganese dioxide are required to liberate the bromine?

✓15. Calculate the weight of chlorine obtained by complete interaction of (a) manganese dioxide, (b) potassium permanganate on 200 g. of sodium chloride in the presence of an excess of sulfuric acid.

✓16. How much sodium chloride can be formed by burning sodium in 25 g. of chlorine?

✓17. How much potassium bromide (95 per cent pure) is necessary for the preparation of 60 g. of bromine?

✓18. What volume of bromine vapor at 100° C. and 760 mm. can be produced from 20 cc. of liquid bromine?

✓19. What volume of chlorine at 10° and 750 mm. will be required to displace all the bromine from 94.5 cc. of a 0.6 normal solution of sodium bromide?

20. What reason have you for thinking that you might increase the solubility of bromine in water by addition of potassium bromide?

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CHAPTER XIII

THE SIMPLE HALOGEN ACIDS

Hydrogen Chloride

History.—Hydrogen chloride is rarely found in nature. Its water solution was known to the alchemists, but its preparation by the action of sulfuric acid on salt was not described until 1648 by Glauber. Its water solution was called "muriatic" acid and is still so referred to commercially. Very few uses for the acid were developed until it became cheap as a by-product of the Le Blanc soda process. A little hydrochloric acid is found in the gastric juice of the stomach.

Preparation.—Under chlorine we have already mentioned the union of hydrogen and chlorine in the light to form hydrogen chloride. This action is explosive, but a jet of chlorine can be burned quietly in an atmosphere of hydrogen. The hydrogen should be present in excess. Some hydrochloric acid is now made commercially by this process. The product is pure and the raw materials, hydrogen and chlorine, may readily be secured by electrolysis of a solution of sodium chloride.

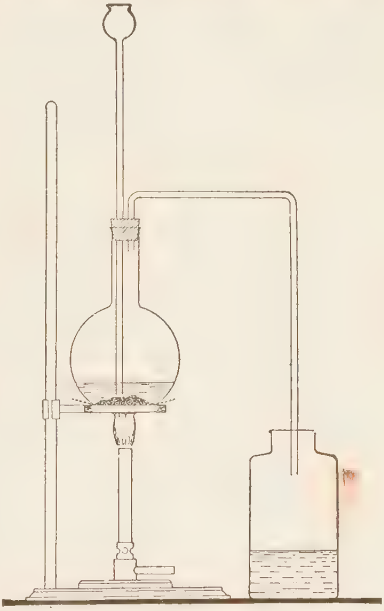


Fig. 62.—Preparation of hydrochloric acid.

The greatest laboratory and commercial method of preparation is the treatment of any suitable choride (sodium chloride is the cheapest) with concentrated sulfuric acid. In practice there is less frothing if the acid is slightly diluted. As shown in Fig. 62

the delivery tube should not quite touch the surface of the water. The gas is so soluble that otherwise water might rush back into the generator:

$$(1)\ NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl.$$

If an excess of salt is used and the temperature raised higher, the reaction is somewhat different:

$$(2)\ 2\ NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ HCl.$$

In (1) sodium hydrogen sulfate is formed and in (2) sodium sulfate (Glauber's salt).

In (1) the hydrogen chloride escapes as gas because it is insoluble in the concentrated sulfuric acid. If, however, rather dilute acid is used, the hydrogen chloride dissolves in the water. When a saturated solution of sodium hydrogen sulfate in water is mixed with concentrated hydrochloric acid, minute cubes of sodium chloride are precipitated.

$$(3)\ NaHSO_4 + HCl \longrightarrow H_2SO_4 + NaCl.$$

This reaction is the exact reverse of (1), so evidently we cannot attribute either to chemical affinity alone. Here the salt precipitates (and the reaction proceeds to the right) because common salt is rather insoluble in concentrated hydrochloric acid. Of course the little crystals are still in contact with sulfuric acid, but the contact is not one millionth as effective as if the salt were really in solution—that is, subdivided into something like single molecules.

The conditions of (1) are therefore radically changed when dilute sulfuric acid is used.

$$NaCl + H_2SO_4 \rightleftarrows NaHSO_4 + HCl.$$

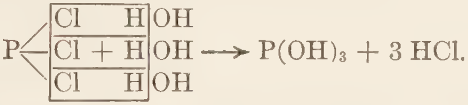
The reaction becomes reversible because there is sufficient water to dissolve the hydrogen chloride. Since it is then in good contact with the sodium hydrogen sulfate, there is nothing to hinder reaction to the left. No gas escapes. It is an impossible method for securing the evolution of hydrogen chloride.

Any metallic chloride serves as well as a source of hydrogen chloride, if it is soluble. Any acid will do if it is less volatile than the hydrogen chloride. For example, H_2F_2, hydrofluoric acid, would be driven off on heating, thus stopping the formation of the hydrogen chloride. The acid used must not react with the desired hydrogen chloride as would nitric or any other oxidizing acid. Phosphoric might seem as good as sulfuric acid, since it also has a higher boiling point than most acids, but unfortunately it reacts too slowly. Sulfuric acid is always used because it is cheap, is less volatile than hydrogen chloride (or most acids, in fact), and does not react with hydrogen chloride.

EXERCISE 1.—Complete

$FeCl_2$ + dilute 2 $H_2SO_4 \longrightarrow Fe(HSO_4)_2 + 2HCl$
$FeCl_2$ + conc. $H_2SO_4 \longrightarrow FeSO_4 + 2HCl$
$3KCl + H_3PO_4 \longrightarrow K_3PO_4 + 3HCl$
$2NaCl + H_2F_2 \longrightarrow Na_2F_2 + 2HCl$
$2AlCl_3$ + conc. $3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 6HCl$

The chlorides of some non-metals react with water to form hydrogen chloride, an example of hydrolysis:



$$P\begin{cases}\boxed{\begin{array}{l} Cl \quad\ H \\ Cl + H \\ Cl \quad\ H \end{array}}\begin{array}{l} OH \\ OH \\ OH \end{array}\end{cases} \longrightarrow P(OH)_3 + 3\,HCl.$$

In the manufacture of nitric acid from sulfuric acid and sodium nitrate a by-product is sodium hydrogen sulfate, $NaHSO_4$. To some extent this is now utilized by heating with salt:

$$NaHSO_4 + NaCl \longrightarrow Na_2SO_4 + HCl.$$

Both the products are valuable, while previously the sodium hydrogen sulfate was a drug on the market.

The simplest method in principle (although not in practice) to make hydrogen chloride is the burning of chlorine in an atmosphere of hydrogen. Combustion takes place as truly as in the oxy-hydrogen blowpipe. Much pure hydrochloric acid is now made commercially by this method in order to utilize the hydrogen escaping as a by-product in the electrolytic manufacture of chlorine and sodium hydroxide from NaCl. On passing the gaseous hydrogen chloride into water an acid solution containing forty per cent (by weight) of HCl is possible, while the other commercial methods yield acids of from 28 to 32 per cent, requiring further concentration. The purity of the direct union product commends it for use in the preparation of certain foods. Common hydrochloric acid sometimes contains arsenic. However made, the hydrogen chloride gas is absorbed in water contained in large stone bottles or in water splashing down through a tower loosely filled with ceramic shapes or coke.

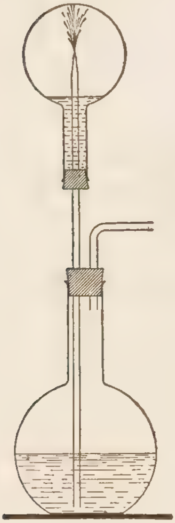


FIG. 63.—Hydrogen chloride fountain.

Physical Properties.—Hydrogen chloride is a colorless gas of choking odor, enormously soluble in water. If the upper flask in Fig. 63 is filled with hydrogen chloride gas introduction of a very little water from below creates a partial vacuum. The gas dissolves quickly in the water and more water rushes in. One volume of water dissolves 455 volumes of the gas at 15° and 760 mm. The solution is called hydrochloric acid. The gas "fumes" in moist air by condensing the invisible moisture into visible droplets of solution. The gas is somewhat heavier than air; one liter weighs 1.642 g. At 0° it is liquefied by 28 atmospheres' pressure, but at −84° one atmosphere liquefies it. This is, then, its boiling point. It freezes at −112.5° and its critical temperature is 52°.

When a concentrated solution is heated it loses hydrogen chloride more rapidly than water until the concentration falls to 20.2 per cent. Then the rest of the liquid distills unchanged at 110°. This product is called the acid of ***constant boiling point.*** If very dilute hydrochloric acid is boiled, steam passes off more rapidly than hydrogen chloride, until the concentration rises to 20.2 per cent. It was once thought this indicated the existence of a compound of hydrogen chloride and water, but by merely changing the pressure the composition of the distillate changes. The "chemically pure" acid has a specific gravity of 1.2 and contains 37 per cent hydrogen chloride and 63 per cent water by weight.

EXERCISE 2.—How many grams of the gas in 850 cc. of "C. P." hydrochloric acid?

Chemical Properties.—As a dry gas hydrogen chloride is not very active, but in water solution it ranks as one of the "strongest" acids. Like all acids, its solution is sour and turns blue litmus paper red.

The metals more active than copper displace hydrogen from hydrochloric acid:

$$Fe + 2\,HCl \longrightarrow FeCl_2 + H_2.$$

Oxides of the metals react with it to form water and a chloride of the metal:

$$Ca\boxed{O + 2\,H}Cl \longrightarrow H_2O + CaCl_2.$$

Hydroxides of the metals (bases) react with hydrochloric acid to form water and metallic chlorides.

$$Na\boxed{OH + H}Cl \longrightarrow H_2O + NaCl,$$

$$Ca\boxed{(OH)_2 + 2\,H}Cl \longrightarrow 2\,H_2O + CaCl_2.$$

The base and acid can be mixed in such proportions that the solution is no longer sour or soapy, or does it affect litmus. We say the acid has ***neutralized*** the base and vice versa.

Nitric acid oxidizes hydrogen chloride into water and chlorine. Another product, nitrosyl chloride, $NOCl$, is also formed:

$$HNO_3 + 3\,HCl \longrightarrow 2\,H_2O + NOCl + Cl_2.$$

A mixture of three volumes of concentrated hydrochloric acid and one volume of concentrated nitric acid is called *aqua regia* because it dissolves gold. Chlorine is continually being released from the mixture and in its atomic state is very active, converting metals to chlorides. It is more efficient in attacking metals and salts than either acid alone.

That hydrogen chloride is a reducing agent is shown by the fact that it can be oxidized.

Uses.—Hydrochloric acid is used to form many chlorides. Many metals, all metallic oxides and hydroxides, and some salts react with it to form chlorides. Carbonates and sulfites of the metals (see below) all react with hydrochloric acid to form chlorides.

$$\begin{aligned} Ca + 2\,HCl &\longrightarrow H_2 + CaCl_2, \\ CaCO_3 + 2\,HCl &\longrightarrow H_2O + CO_2 + CaCl_2, \\ Na_2SO_3 + 2\,HCl &\longrightarrow H_2O + SO_2 + 2\,NaCl, \\ AgNO_3 + HCl &\longrightarrow HNO_3 + AgCl. \end{aligned}$$

In the third reaction the silver chloride formed is insoluble and therefore gives a precipitate if formed in a solution. It is one of the three insoluble chlorides, the other two being mercurous chloride and lead chloride. They are worth remembering.

Hydrogen chloride has its greatest use as a source of chlorine by oxidation.

It is used, also, to clean metals (reacting with the oxide, rust).

Test.—A solution turning blue litmus red and forming a white precipitate of silver chloride when silver nitrate is added must contain hydrogen chloride. As a gas it can be detected by holding a drop of silver nitrate solution on a glass rod in the air. A milkiness in the drop is a test, confirmed by the reddening of moist blue litmus paper.

Hydrogen Bromide, Hydrogen Iodide, and Hydrogen Fluoride

The Simple Halogen Acids.—H_2F_2, HBr, and HI, resemble HCl in many respects. All are colorless gases, irritating in odor, extremely soluble in water, forming acid solutions, and fuming in moist air. They may all be made by direct union of the elements, but with certain differences. In practice hydrogen fluoride is made by warming concentrated sulfuric acid and calcium fluoride in a lead vessel as glass is attacked:

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2F_2.$$

We might reasonably expect hydrogen bromide to be made by treating a bromide with concentrated sulfuric acid:

$$(1)\ NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr.$$

Yet when we do this we observe a red-brown gas in addition to the colorless, fuming hydrogen bromide. A paper wet with starch and potassium iodide solutions turns blue. From this and the color and the choking, irritating odor we decide that bromine was released, evidently oxidized out of the hydrogen bromide by the concentrated sulfuric acid. When dilute sulfuric acid is used, no gas escapes and no color appears. The reaction becomes reversible as with chlorides because of the great solubility in water of hydrogen bromide. But it is noteworthy that no red-brown color can be seen—dilute sulfuric acid is not an oxidizing agent. With concentrated acid equation (1) is followed by (2):

$$(2)\ 2\,HBr + H_2SO_4 \longrightarrow 2\,H_2O + SO_2 + Br_2.$$

Each molecule of hot, concentrated H_2SO_4 loses one oxygen atom to the hydrogen of the bromide and leaves H_2SO_3, which is unstable, yielding $H_2O + SO_2$.

Pure hydrogen bromide can be made by warming

$$KBr + H_3PO_4 \longrightarrow KH_2PO_4 + HBr$$

because phosphoric acid is not an oxidizing agent. Like sulfuric acid it has a high boiling point.

We might also have expected to make hydrogen iodide by warming some iodide with concentrated sulfuric acid:

$$NaI + H_2SO_4 \longrightarrow NaHSO_4 + HI.$$

Very little fuming in moist air shows the presence of but little hydrogen iodide. Much violet vapor proves to be free iodine. As with the bromide, concentrated sulfuric acid oxidizes the hydrogen iodide:

$$2\ HI + H_2SO_4 \longrightarrow 2\ H_2O + SO_2 + I_2.$$

A vile odor of rotten eggs indicates the presence of hydrogen sulfide (H_2S), so some molecules of sulfuric acid must have given up all four oxygen atoms for the work of oxidation. This really means that hydrogen iodide is a more vigorous reducer than hydrogen bromide:

$$8\ HI + H_2SO_4 \longrightarrow 4\ H_2O + 4\ I_2 + H_2S.$$

So we discard the sulfuric acid method as unsuitable for hydrogen bromide or iodide. Phosphoric acid would be excellent, as it is not very volatile and is not an oxidizing acid, but unfortunately the action is too slow. If the temperature is raised to increase the speed, the product decomposes:

$$2\ HI \longrightarrow H_2 + I_2.$$

The Electronic Balancing of Oxidation Equations.—As stated before (page 159), *oxidation is the loss of electrons and reduction the gaining of electrons.* Naturally, when one substance oxidizes a second substance the number of electrons lost by the first must equal the number gained by the second and on this basis the balancing of oxidation-reduction equations is clearly understood. Brinkley, in his *General Chemistry,* puts this well, so we illustrate the method by quoting his discussion of the oxidation of hydrogen bromide and hydrogen iodide by concentrated sulfuric acid. He first sets down an unbalanced equation representing the reacting substances and the known products. Next he shows the valence drop in passing of the hexavalent positive sulfur (of H_2SO_4) to tetravelent positive sulfur (of SO_2, a product) in terms of gain of electrons by the sulfur (the H_2SO_4 is itself reduced). A similar setting down of electron loss (oxidation) of the bromine (in the HBr) leads to counting of a balance between gain and loss of electrons. That the sulfur in H_2SO_4 has a valence of six is evident if you consider its anhydride, SO_3. Removal of H_2O from H_2SO_4 involves no valence change.

Remember that oxidation of an element (or compound) is loss of electrons and resultant increase in the positive valence. Conversely, reduction is essentially the gain of electrons with resultant decrease in positive valence by the element reduced.

$$\begin{array}{ll} \text{``}HBr + H_2SO_4 \rightarrow H_2O + Br_2 + SO_2. & \text{(Unbalanced)} \\ H_2SO_4 \rightarrow SO_2;\ S^{6+} \rightarrow S^{4+}; & \text{Gain } 2(-) \\ 2\ HBr \rightarrow Br_2;\ 2\ Br^- \rightarrow Br_2^\circ; & \text{Loss } 2\ (-) \end{array}$$

Hence, 2 molecules of hydrobromic acid are oxidized by 1 molecule of sulfuric acid and the balanced equation is,

$$2\ HBr + H_2SO_4 \rightarrow 2\ H_2O + Br_2 \uparrow + SO_2 \uparrow.$$

Hydriodic acid is less stable and, therefore, a better reducing agent than hydrobromic acid. The reduction of sulfuric acid goes further in this case, and free sulfur and hydrogen sulfide, as well as some sulfur dioxide, may be recognized as products of the reaction of sulfuric acid with the displaced hydriodic acid.

$$\begin{array}{ll} HI + H_2SO_4 \rightarrow H_2S + I_2 + H_2O & \text{(Unbalanced)} \\ H_2SO_4 \rightarrow H_2S;\ S^{6+} \rightarrow S^{2-}; & \text{Gain } 8\ (-) \\ 2\ HI \rightarrow I_2;\ 2\ I^- \rightarrow I_2^\circ; & \text{Loss } 2\ (-) \end{array}$$

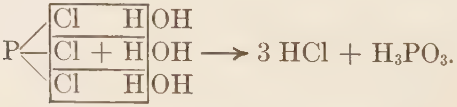
Four molecular proportions of iodine are formed for each molecule of sulfuric acid reduced to hydrogen sulfide, and the balanced equation is,

$$8\ HI + H_2SO_4 \rightarrow H_2S \uparrow + 4\ I_2 + 4\ H_2O.\text{''}$$

Schlesinger in his *General Chemistry*, page 276, balances such equations by use of a somewhat diagrammatic gain and loss of electrons.

The Red Phosphorus Method.—The red phosphorus method, however, serves us very well. It is recalled that chlorine and phosphorus unite to form a chloride, PCl_3, that is hydrolyzed by water:

$$\begin{aligned} PCl_3 + 3\ H_2O &\longrightarrow P(OH)_3 + 3\ HCl, \\ PBr_3 + 3\ H_2O &\longrightarrow P(OH)_3 + 3\ HBr, \\ PI_3 + 3\ H_2O &\longrightarrow P(OH)_3 + 3\ HI, \end{aligned}$$



$$P\begin{cases} \boxed{\begin{array}{l} Cl \quad H \\ Cl + H \\ Cl \quad H \end{array}} \begin{array}{l} OH \\ OH \\ OH \end{array} \end{cases} \longrightarrow 3\ HCl + H_3PO_3.$$

The reactions with phosphorus tribromide and phosphorus triiodide are similar. Red phosphorus, slightly moistened, is put in a flask with a delivery tube attached, and bromine cautiously added from a dropping funnel. The heat of the reaction volatilizes much bromine, which is caught by a little moist red phosphorus in a U-tube through which the gases pass (Fig. 64). The colorless hydrogen bromide is led into water, forming hydrobromic acid. Of course the first reaction was as follows:

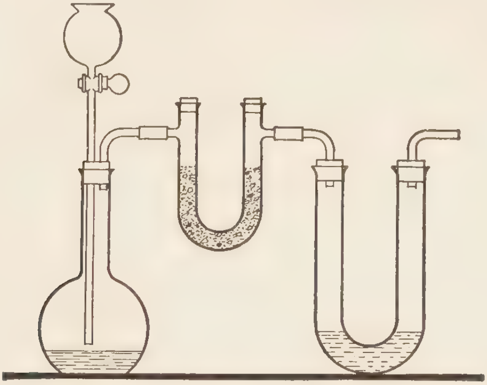


FIG. 64.—The red phosphorus method of making hydrogen bromide.

$$2\ P + 3\ Br_2 \longrightarrow 2\ PBr_3.$$

With hydrogen iodide the water is dropped on a mixture of red phosphorus and iodine. Hydrogen sulfide passed into water containing iodine in suspension reacts as follows:

$$H_2S + I_2 \longrightarrow 2\ HI + S.$$

The sulfur may be filtered out and the colorless liquid concentrated by boiling. Anhydrous hydrogen iodide is then obtained if the solution is dropped on phosphorus pentoxide, which combines with the water.

Bromine reacts with benzene to form hydrogen bromide:

$$C_6H_6 + Br_2 \longrightarrow C_6H_5Br + HBr.$$

The Catalytic Formation of Halogen Acids.—That the halogens are made more reactive by contact with carbon is indicated by the passage of a molecular mixture of H_2 and Br_2 gases over ultraporous charcoal at 200°. Fully 99.3 per cent of the gases unite to form HBr. Without the carbon practically no reaction takes place. The formation of HCl and of HI is similarly catalyzed by carbon. Platinum is also an effective catalyst for these reactions.

Properties of the Halogen Acids.—These colorless, extremely soluble gases have all been liquefied at low temperatures, but are not acid unless mixed with water. The explanation of this is given in the chapter on Ionization. The water solutions are called hydrobromic acid, hydriodic acid, and hydrofluoric acid. As such they are very strong acids and conduct electricity well. They react with most metals with displacement of hydrogen, and react with metallic oxides and hydroxides as does hydrochloric acid:

$$\begin{aligned} Zn + 2\,HBr &\longrightarrow ZnBr_2 + H_2, \\ MgO + 2\,HBr &\longrightarrow MgBr_2 + H_2, \\ NaOH + HI &\longrightarrow NaI + H_2O, \\ CaCO_3 + 2\,HBr &\longrightarrow CaBr_2 + H_2O + CO_2. \end{aligned}$$

Exercise 3.—How would you make $CaBr_2$ five ways? How would you make NaI five ways? Compare with page 179.

From the foregoing discussion it is clear that we have not oxidized hydrogen fluoride at all by any reagent; that hydrogen chloride is not oxidized by concentrated sulfuric acid but can be attacked by several better oxidizing agents; that hydrogen bromide is so easily oxidized that even hot concentrated sulfuric acid does it; and that hydrogen iodide is still more easily oxidized. A solution of hydriodic acid soon turns red because free oxygen of the air reacts with part of it.

$$\begin{aligned} &(1)\quad 4\,HI + O_2 \longrightarrow 2\,H_2O + 2\,I_2, \\ &(2)\quad I_2 + HI \rightleftarrows HI_3. \end{aligned}$$

Reaction (2) is suggestive of the solution of iodine in potassium iodide.

It is a general principle that compounds with higher heat of formation are most stable.

Heat of formation of HF is 38,600 cal.
Heat of formation of HCl is 22,000 cal.
Heat of formation of HBr is 8,400 cal.
Heat of formation of HI is −6,000 cal.

Anhydrous hydrogen bromide boils at −68.5°, hydrogen iodide at −36°, and hydrogen fluoride at 19°. Hydrogen fluoride gas is very poisonous. The density of hydrogen fluoride gas indicates a molecular weight of 40 and hence the formula H_2F_2, but this has been explained by the existence of a mixture of HF and H_6F_6. Above 100° the density indicates a formula of HF.

Uses of the Acids.—Hydrobromic and hydriodic acids have little commercial use, but hydrofluoric acid is valuable because it etches glass. Common glass is a mixture of the silicates of sodium and calcium.

$$Na_2SiO_3 + 3\ H_2F_2 \longrightarrow Na_2F_2 + SiF_4 + 3\ H_2O,$$
$$CaSiO_3 + 3\ H_2F_2 \longrightarrow CaF_2 + SiF_4 + 3\ H_2O.$$

Bottles, thermometers, etc., are marked by covering with a film of paraffin, cutting through a design, and then exposing the vessels to the fumes or the liquid acid. The wax is not attacked but the glass is etched where the scratches expose it. Later the vessel is washed and the wax melted. A 30 per cent solution of the acid is commonly used. Rubber, lead, bakelite, or ceresin-wax bottles are the common containers, since this acid cannot be kept in glass bottles.

This acid is used in aiding glass polishers to make "cut" glass, in cleaning sand from metal castings, and in removing silica from straw used for hats so as to make the straw more flexible. The action on silica or sand is

$$SiO_2 + 2\ H_2F_2 \longrightarrow 2\ H_2O + SiF_4.$$

Tests for the Halogens.—Free chlorine is recognized by its odor, yellow color, and its ability to displace iodine from any soluble iodide.

$$2\ KI + Cl_2 \longrightarrow 2\ KCl + I_2.$$

If starch is present, the free iodine with the starch forms a blue compound (or solution).

Free bromine is known by its red-brown color, its odor, and its ability to displace iodine from any soluble iodide. The usual blue with starch can easily be secured.

$$2\ KI + Br_2 \longrightarrow 2\ KBr + I_2.$$

Free iodine with its violet-black color and its formation of a blue compound when in contact with starch is easily recognized. Furthermore its solution in carbon disulfide shows a beautiful violet color.

A soluble chloride reacts with a solution of silver nitrate to give a white precipitate of silver chloride darkening in the light. A soluble bromide with silver nitrate gives insoluble yellow-white silver bromide. A soluble iodide with silver nitrate precipitates canary-yellow silver iodide. Furthermore, chlorine water displaces bromine from a bromide and iodine from an iodide.

Preparation of Salts.—Illustrations of various methods of preparing salts are:

1. $Ca + Cl_2 \longrightarrow CaCl_2$,
2. $Ca + 2\,HCl \longrightarrow H_2 + CaCl_2$,
3. $CaO + 2\,HCl \longrightarrow H_2O + CaCl_2$,
4. $Ca(OH)_2 + 2\,HCl \longrightarrow 2\,H_2O + CaCl_2$,
5. $CaCO_3 + 2\,HCl \longrightarrow H_2O + CO_2 + CaCl_2$,
6. $CaSO_3 + 2\,HCl \longrightarrow H_2O + SO_2 + CaCl_2$,
7. $CaO + SiO_2 \longrightarrow CaSiO_3$,
or $CaO + SO_3 \longrightarrow CaSO_4$,
8. $CaCl_2 + Na_2SO_4 \longrightarrow 2\,NaCl + CaSO_4\downarrow$.

EXERCISES

4. When hydrogen chloride (in solution) is electrolyzed, equal volumes of hydrogen and chlorine are obtained. Also when equal volumes of hydrogen and chlorine are combined, two volumes of hydrogen chloride are formed. How does this confirm Gay-Lussac's law?

5. Balance:

$PbO + HCl \rightarrow$
$Pb_2O_3 + HCl \rightarrow$
$Pb_3O_4 + HCl \rightarrow$
$PbO_2 + HCl \rightarrow$
$MnO + HCl \rightarrow$
$Mn_2O_3 + HCl \rightarrow$
$Mn_3O_4 + HCl \rightarrow$
$MnO_2 + HCl \rightarrow$
$Na_2CO_3 + HCl \rightarrow$
$CuO + HCl \rightarrow$
$KOH + HCl \rightarrow$

6. How many liters of chlorine are released by heating 2 Kg. of red lead, Pb_3O_4, with enough hydrochloric acid to complete the reaction?

7. Make zinc chloride five ways. Equations. Make zinc sulfate four ways. Give four general methods of preparing any salt desired.

8. Suppose you wished to prepare 1000 g. of hydrobromic acid containing 10 per cent by weight of HBr. Calculate the weights of the various compounds that you would use in its preparation.

9. What volume of HBr gas at 20° and 745 mm. will be obtained by adding water to 10 g. of phosphorus tribromide?

10. How much (a) calcium sulfate and (b) hydrogen fluoride are formed by heating 75 g. of fluorspar with sulfuric acid?

CHAPTER XIV

THE OXYGEN ACIDS OF THE HALOGENS

Chlorine and iodine do not combine directly with oxygen, but their oxides can be made by indirect methods. Bromine and fluorine have no oxides, and fluorine has no place in this chapter at all, for it forms neither oxide nor oxygen acid.

Hypochlorous Acid.—The key reaction of this entire chapter has been studied in the chlorine chapter:

✓
$$(1)\quad Cl_2 + H_2O \rightleftharpoons HCl + HOCl.$$

This is shown to be a reversible reaction by tests for acidity and for the presence of free chlorine. Blue litmus paper is reddened before it is bleached, but the solution is only weakly acid. The presence of dissolved chlorine is proved by the yellow color of the mixture, by odor, and by the reaction on a starch-potassium iodide paper. (What is this reaction?) The hypochlorous acid (HOCl) is a powerful oxidizing agent and so the equilibrium is disturbed to the right by the presence of any oxidizable substance. Addition of a base also disturbs the equilibrium to the right by conversion of the two acids into salts. (The equilibrium condition in bromine water is disturbed in similar manner by addition of a base.)

$$(2)\quad NaOH + HCl \longrightarrow H_2O + NaCl,$$
$$(3)\quad NaOH + HOCl \longrightarrow H_2O + NaOCl.$$

In other words there is no free chlorine left in the solution after sufficient base has been added. The bleaching power of such a solution was first observed by Berthollet in 1785. Chlorine passed into sodium hydroxide solution forms, then, sodium chloride and sodium hypochlorite (NaOCl), sometimes called Javelle water.

If to the mixture represented by (2) and (3) sufficient dilute sulfuric acid is added, both hydrochloric and hypochlorous acids are formed:

$$(4)\quad NaCl + H_2SO_4 \rightleftharpoons NaHSO_4 + HCl,$$
$$(5)\quad NaOCl + H_2SO_4 \rightleftharpoons NaHSO_4 + HOCl,$$
$$(6)\quad HCl + HOCl \rightleftharpoons H_2O + Cl_2.$$

Reaction (6) inevitably follows (4) and (5). It is simply the reverse of (1). No wonder chlorine can be detected after acidifying Javelle water.

Hypochlorous acid is a more energetic oxidizing agent than oxygen because more energy is released by the oxidation of a given weight of some reducing substance in the first case than in the second. Hypochlorous acid is a valuable bleaching agent from the very fact that it bleaches by oxidation of coloring matter.

On concentrating this unstable acid too far it decomposes into water and its anhydride, chlorine monoxide.

$$2\ HOCl \rightleftharpoons H_2O + Cl_2O.$$

An ***anhydride*** of an acid is an oxide that reacts with water to form the acid and it may be represented by the formula of the acid less the elements of water. SO_3 is the anhydride of H_2SO_4. To get the anhydride of nitric acid we must subtract H_2O from $2\ HNO_3$. An anhydride of a base is an oxide that reacts with water to form the base. CaO is the anhydride of $Ca(OH)_2$.

Exercise 1.—What is the anhydride of carbonic acid (H_2CO_3)? Of phosphoric acid (H_3PO_4)?

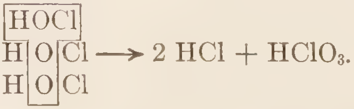
In the chlorine chapter we learned that hypochlorous acid decomposes slowly in the sunlight:

$$2\ HOCl \longrightarrow 2\ HCl + O_2.$$

Even its salts are somewhat unstable, decomposing slowly thus:

$$2\ NaOCl \longrightarrow 2\ NaCl + O_2.$$

"Dakin's solution," used for sterilizing deep wounds, is really sodium hypochlorite. A stabilized form of this salt is sold under various commercial names for antiseptic purposes.



$$\begin{array}{l} \boxed{HOCl} \\ H\,\boxed{O}\,Cl \longrightarrow 2\ HCl + HClO_3. \\ H\,\boxed{O}\,Cl \end{array}$$

The free acid decomposes in another way, as shown by the equation above. The sodium salt reacts in similar fashion, especially in a hot, concentrated, slightly acid solution, and sodium chlorate is formed rapidly:

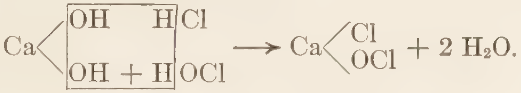
$$3\ NaOCl \longrightarrow 2\ NaCl + NaClO_3.$$

This remarkable reaction reminds us of three brothers, each too poor to boast. But two self-sacrificing ones gave all their money to the third, enriching him to a degree that brought luster to the family name. Most absurd but a clear parallel to the auto-oxidation of the 3 NaOCl.

over concentrating
sunlight
H_2O form $HClO_3$ + t

EXERCISE 2.—In what three ways can hypochlorous acid decompose?

✓ **Bleaching Powder.**—Lime may be used instead of sodium hydroxide to react with chlorine and, if done in the dry form, a ***bleaching powder*** results:



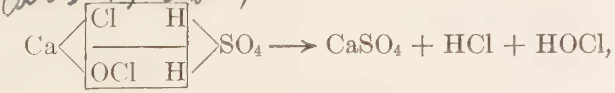
$$Ca\begin{matrix}\diagup OH \quad H|Cl \\ \diagdown OH + H|OCl\end{matrix} \longrightarrow Ca\begin{matrix}\diagup Cl \\ \diagdown OCl\end{matrix} + 2\ H_2O.$$

In all probability a little water in the dry powder reacts with chlorine to form the two acids, as in equation (1). Of course they promptly neutralize the lime and more water is formed.

Bleaching powder is sometimes called "chloride of lime," which should refer only to $CaCl_2$. It was once thought to be a mixture of an equal number of molecules of $CaCl_2$ and $Ca(OCl)_2$. This is incorrect, however, because alcohol dissolves nothing from it and yet calcium chloride is very soluble in alcohol. Furthermore, calcium chloride is very deliquescent, and commercial bleaching powder is not. It is evidently a mixed salt of both hydrochloric and hypochlorous acids, as indicated by the formula $Ca\begin{matrix}\diagup Cl \\ \diagdown OCl\end{matrix}$.

When acidified the reaction resembles the one with acidified Javelle water:

$CaCl_2O + H_2SO_4$



$$Ca\begin{matrix}\diagup Cl \quad H \diagdown \\ \diagdown OCl \quad H \diagup\end{matrix}SO_4 \longrightarrow CaSO_4 + HCl + HOCl,$$

$$HCl + HOCl \rightleftarrows H_2O + Cl_2.$$

As stated before, it is the hypochlorous acid that does the bleaching. The question naturally arises: How is it that bleaching powder always smells of chlorine when no acid has been added?

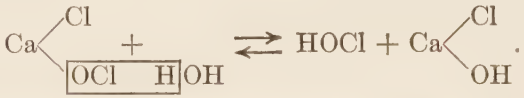
$CaCl_2O + HCl \rightarrow CaCl_2 + HClO$

$HClO \rightarrow \underline{O} + HCl$

heating, bleaching in

The fact is this odor is not due to chlorine but to chlorine monoxide (Cl_2O). The small amount of carbonic acid always present in the air (from $H_2O + CO_2 \rightleftarrows H_2CO_3$) is able to release the hypochlorous acid but not the hydrochloric acid. Hypochlorous acid is unstable and to some extent decomposes into water and its anhydride, chlorine monoxide, which smells like chlorine.

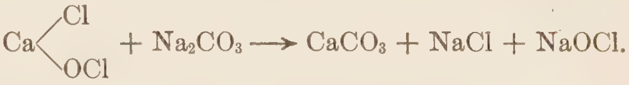
It is also probable that the reaction of water with bleaching powder (hydrolysis) releases a little hypochlorous acid and basic calcium chloride:



$$Ca\begin{cases}Cl\\ \boxed{OCl\quad H}OH\end{cases} + \rightleftarrows HOCl + Ca\begin{cases}Cl\\ OH\end{cases}.$$

For reasons developed later very little hydrochloric acid is released. The foregoing discussion explains why clothes can be bleached by wetting with a solution of bleaching powder and hanging in the air and sunlight.

The best modern laundry practice discourages the direct use of bleaching powder and uses Javelle water made by the reaction:



$$Ca\begin{cases}Cl\\ OCl\end{cases} + Na_2CO_3 \longrightarrow CaCO_3 + NaCl + NaOCl.$$

The insoluble calcium carbonate is filtered off.

Warming a suspension of bleaching powder with a little of some cobalt or nickel salt present yields a steady stream of oxygen gas.

NOMENCLATURE

Metals or Elements with a variety of valence - upper right corn

Oxyhalogen Acids

HCl	Hydrochloric Acid	$NaCl$	Sodium Chloride	HBr	Hydrobromic Acid	HI	Hydriodic Acid
$HOCl$	Hypochlorous Acid	$NaOCl$	Sodium Hypochlorite	$HOBr$	Hypobromous Acid	HOI	Hypoiodous Acid
$HClO_2$	Chlorous Acid	$NaClO_2$	Sodium Chlorite	....		....	
$HClO_3$	Chloric Acid	$NaClO_3$	Sodium Chlorate	$HBrO_3$	Bromic Acid	HIO_3	Iodic Acid
$HClO_4$	Perchloric Acid	$NaClO_4$	Sodium Perchlorate	....		HIO_4	Periodic Acid

ic, ous = adj end.
per - more.
hypo - less than

The manufacture of bleaching powder is a huge industry. Chlorine is passed over three-inch layers of slaked lime ($Ca(OH)_2$) which are stirred occasionally. In theory the product should contain 49 per cent of "available" chlorine (liberated by acids), but in practice from 35 to 38 per cent is the best obtained, about two thirds efficiency.

In the table given above is a fine illustration of the law of Multiple Proportions.

Chloric Acid.—One of the most important of the oxygen acids of the halogens is chloric acid ($HClO_3$). It can be made by the action of dilute sulfuric acid on any chlorate, preferably barium chlorate, because the by-product, barium sulfate, is insoluble and can be filtered off:

$$Ba(ClO_3)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2\ HClO_3.$$

This vigorous oxidizing acid is a colorless liquid which can be concentrated to a 40 per cent solution without decomposition if kept below 40°. It is really a more energetic oxidizing agent than ozone.

When a few drops of concentrated sulfuric acid are added to two or three fragments of potassium chlorate the size of grains of wheat, the chloric acid freed decomposes violently:

$$4\ HClO_3 \longrightarrow 2\ H_2O + O_2 + 4\ ClO_2.$$

It is dangerous to use larger quantities. A hot wire thrust into the chlorine dioxide gas escaping causes a very violent explosion.

In a way, chloric acid is used as the norm in naming these acids. An acid with more oxygen is called perchloric; the one with a little less is called chlorous acid; one with still less hypochlorous acid; and the one with no oxygen at all has a different style of name. In the corresponding salts the ending "ate" goes with the ending "ic" in the oxygen acid and the ending "ite" with the ending "ous" in the acid. There are only three oxides of chlorine, namely chlorine monoxide (Cl_2O), chlorine dioxide (ClO_2), and chlorine heptoxide (Cl_2O_7). There are no oxides of bromine. Iodine has two oxides, the pentoxide (I_2O_5) and the heptoxide (I_2O_7).

The ***structural formulas*** of the oxygen acids of chlorine are worth noting.

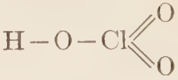
Hypochlorous Acid

$H-O-Cl$

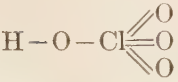
Chlorous Acid

$H-O-Cl=O$

Chloric Acid



Perchloric Acid



So far we have considered the valence of chlorine as one, but here we see that it may also be three, five, or seven. Chlorine heptoxide (Cl_2O_7) indicates a valence of seven as it should be in the anhydride of perchloric acid.

Chlorates.—More important than chloric acid is its potassium salt ($KClO_3$). This finds use as a convenient laboratory source of oxygen and in the manufacture of fireworks, matches, dyes, and explosives. It is such an effective source of oxygen that the results of its use are often startling and sometimes dangerous.

It is interesting to drop a splinter into a test tube one third full of melted potassium chlorate. So vigorous is the oxidation of the wood that it burns brilliantly under the liquid, flames shoot out of the tube, and some spattering of hot liquid may result. Were the wood finely divided as sawdust or used as powdered charcoal, a dangerous explosion would result.

One chemist grinding pure potassium chlorate in a clean mortar was astonished by a loud explosion. Another mortar from the same lot produced the same result. Investigation showed that the wooden handle of the pestle had been cemented into the head by melted sulfur. The sulfur crumbled and a little fell into the potassium chlorate during grinding. The enormously rapid oxidation of sulfur was explosive.

The simplest method of making potassium chlorate is to pass chlorine into a hot, concentrated solution of potassium hydroxide:

$$3\ Cl_2 + 6\ KOH \longrightarrow KClO_3 + 5\ KCl + 3H_2O.$$

This equation sums up several steps. First chlorine reacts with water, then the acids formed are neutralized by the base and finally potassium hypochlorite is partly converted into the desired chlorate—as it does rapidly if the solution is hot:

$$3\ KClO \longrightarrow 2\ KCl + KClO_3.$$

Potassium hydroxide is not cheap, yet in this method five sixths of it is almost wasted, becoming the far cheaper potassium chloride. An economy long ago adopted was to pass chlorine first into a suspension of lime in water and thus secure the cheaper calcium salts:

$$6\ Ca(OH)_2 + 6\ Cl_2 \longrightarrow 5\ CaCl_2 + Ca(ClO_3)_2 + 6\ H_2O,$$
$$Ca(ClO_3)_2 + 2\ KCl \longrightarrow CaCl_2 + 2\ KClO_3.$$

Here the five-sixths waste is in cheap calcium hydroxide and only enough potassium chloride is added later to convert the calcium chlorate into potassium chlorate. The latter salt is easily separated from the more soluble calcium chloride.

The most modern method of manufacture is to electrolyze potassium chloride, letting the solutions at the anode and cathode mix. This first produces the hypochlorite, but if the solutions are hot and concentrated the chlorate is the final product.

The Perchlorates.—The most surprising property of perchloric acid and its salts is their stability. Especially is this true of the perchlorates of the alkali and alkaline-earth metals. Probably the most stable of these is lithium perchlorate. It has been shown to be perfectly stable at 400° C., within 100 degrees of a visible red heat—a remarkable stability for a substance containing well over fifty per cent of its weight of oxygen. Its oxygen content can be liberated as gas if sufficient heat is applied, and the reaction is not violent. Lithium perchlorate has been used with the best attainable results in the determination of the atomic weight of silver. Barium perchlorate is almost as stable, although it contains a smaller percentage of oxygen.

The perchlorates, almost without exception, are soluble not only in water, but in practically all organic solvents. Not only are they soluble, but extremely so, solutions of sirupy consistency being the rule. Perchlorates are universally soluble in a degree equaled by no other known series of salts. Moreover, solutions of the perchlorates in all solvents have a very marked temperature coefficient of solubility. A tenfold increase in solubility for a rise of 100 degrees is not uncommon.

Furthermore, the metallic perchlorates are practically all deliquescent in no moderate degree. Anhydrous magnesium perchlorate absorbs water with an avidity known to no other material which absorbs by means other than true chemical reaction. The most thorough drying agent known, the anhydride of phosphoric acid, represents a different type of drying agent, and anhydrous magnesium perchlorate is its equal in efficiency and greatly its superior in capacity. Other perchlorates, in particular barium perchlorate, are almost the equal of the magnesium salt as a water absorbent.

Potassium perchlorate has recently been substituted for potassium chlorate as a safer accelerator for the Parr peroxide bomb calorimeter. If potassium chlorate is heated only until about one-fifth of its oxygen is lost a good deal of perchlorate will be obtained.

$$4\ KClO_3 \longrightarrow 3\ KClO_4 + KCl.$$

Heating of $KClO_3$

There are three forms of perchloric acid but the one readily prepared, approximately $HClO_4 \cdot 2\ H_2O$, is quite stable in the constant boiling concentration of 72.4 per cent.

The periodates (salts of HIO_4) are made by first electrolytically oxidizing iodic acid, HIO_3, in a nitric acid solution, using an anode of lead dioxide.

EXERCISES

3. Calculate the weight of potassium perchlorate which could be formed from 12.25 g. of potassium chlorate if no decomposition to evolve oxygen occurs.

4. Suppose you electrolyzed 70 g. of potassium chloride in an apparatus so arranged that the chlorine set free at the anode would react with the potassium hydroxide formed at the cathode. What weight of potassium chlorate would be formed?

5. What weight of potassium chlorate will be obtained by the action of excess chlorine on 400 cc. 6 N. KOH (warm), assuming that only an 80 per cent recovery of the pure salt is possible?

6. When sufficient NaOH or other base is added to bromine water the red color disappears. Explain.

7. What are the anhydrides of all the oxygen acids of the halogens?

8. Why is it dangerous to add concentrated sulfuric acid to several grams of potassium chlorate?

9. Make out a list of all the oxidizing agents mentioned so far. Also a list of all the reducing agents.

10. Why not prepare potassium chlorate commercially by passing chlorine directly into potassium hydroxide?

11. If a mixture of sulfur and potassium chlorate were ignited (don't do it), what reaction would take place?

CHAPTER XV

SODIUM AND SODIUM HYDROXIDE. BASES

Occurrence of Sodium.—There is slightly less sodium than potassium in the earth's crust, but most sodium minerals are soluble, while soluble potassium minerals are scarce. Sodium chloride is the starting point for most of our prepared sodium compounds. There are also important deposits of sodium nitrate, sodium sulfate, sodium carbonate, borax, and albite feldspar.

Preparation.—Sir Humphry Davy was the first to prepare sodium. He electrolyzed moist sodium hydroxide and collected the metal at the cathode. In the same year (1807) he made potassium from its hydroxide. The high cost of electricity for many years hindered the commercial development of Davy's discovery. During this period the metal was prepared by reduction of the carbonate or hydroxide:

$$Na_2CO_3 + 2\ C \longrightarrow 3\ CO + 2\ Na.$$

With cheap electricity Davy's method was revived, in modified form. Castner's method, now much used, is to electrolyze fused sodium hydroxide in an iron vessel with the cathode (an iron rod) under a bell or inverted iron box (Fig. 65). The metal floats to the surface under this bell and is protected from the air by the hydrogen which is also liberated at the cathode. From time to time the hydrogen escapes by lifting the lid of the bell. Oxygen is released at the iron anodes. A wire gauze keeps the drops of sodium in the cathode compartment. Good commercial practice calls for a temperature as close to the melting point of the hydroxide (300°) as possible. At 325° the sodium is lost by reaction with

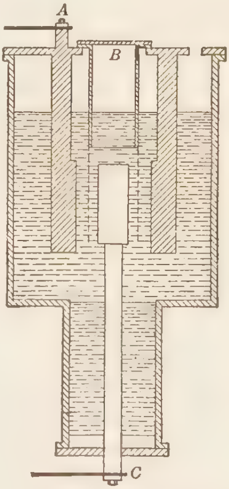


Fig. 65.—Preparation of sodium by electrolysis of fused, dry sodium hydroxide.

the hydroxide, while at 300° the yield is good:

$$2\ Na + 2\ NaOH \longrightarrow H_2 + 2\ Na_2O.$$

Sodium hydroxide melts at 300° and sodium chloride at 803°, so it is easy to see why the hydroxide is electrolyzed.

Properties.—Sodium is silver-white, soft, and lighter than water. It melts at 97° and boils at 877.5°. The vapor is blue and its solution in anhydrous liquefied ammonia is also blue. Like the similar blue potassium solution, this remarkable liquid conducts electricity *without decomposition.* The beautiful blue color of some specimens of rock salt is due to minute particles of the free metal dispersed in the salt (a solid colloidal suspension). Sodium is very active, reacting violently with water. In a somewhat similar way it displaces hydrogen from alcohol:

$$2\ H_2O + 2\ Na \longrightarrow 2\ NaOH + H_2,$$
$$2\ C_2H_5OH + 2\ Na \longrightarrow 2\ C_2H_5ONa + H_2.$$

It unites with oxygen in the cold and burns if heated in oxygen or air. With the halogens reaction readily occurs.

Sodium amalgam is a solution of sodium in mercury (really an alloy). With plenty of sodium the solution is a solid. Its action on water is moderated by the mercury, so the alloy is a useful reducing agent. An alloy of lead and sodium is quite similar. Most of the sodium now made is used to prepare the peroxide and cyanide. A century ago sodium was used in the liberation of aluminum metal from its chloride but a cheaper process was discovered.

Sodium Hydroxide, NaOH.—This important substance is a white brittle solid. It is very soluble in water and is quite deliquescent. Sticks exposed to the air rapidly take up water and carbon dioxide. For this reason it is often used to absorb carbon dioxide in analysis and as a drying agent. To purify the hydroxide it is sometimes dissolved in alcohol. Any carbonate present remains undissolved. The purest product, however, is prepared by cautious addition of sodium to water. There are obvious objections to this method. Much sodium hydroxide is still made commercially by treating boiling soda solutions with slaked lime in some excess:

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2\ NaOH.$$

The precipitated calcium carbonate is filtered off and the filtrate concentrated. The more modern method, however, is the electrolysis of sodium chloride solutions

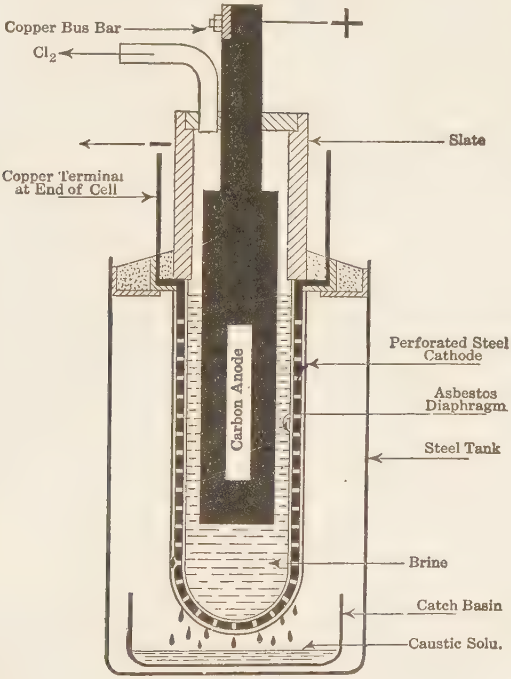

Copper Bus Bar
Cl_2
+
Slate
Copper Terminal at End of Cell
Perforated Steel Cathode
Asbestos Diaphragm
Carbon Anode
Steel Tank
Brine
Catch Basin
Caustic Solu.

Fig. 66.—Nelson cell for the manufacture of sodium hydroxide by electrolysis of salt water.

The Nelson cell (Fig. 66) is one of the leading cells. It belongs to the diaphragm type. The graphite anodes are separated from the cathode, a perforated steel plate, by a porous diaphragm of asbestos. An inverted box of slate over the anodes collected the chlorine. The cell body is a steel tank with an outlet for the sodium hydroxide solution. A current of steam may be led through the cathode compartment to speed up diffusion. Salt brine flows steadily into the anode compartment. The out-flowing solution contains 10 to 12 per cent sodium hydroxide and 14 to 16 per cent of salt, which is precipitated by partial evaporation. This is a simple matter because salt is much less soluble than the hydroxide. The cells are rated at 1000 amperes and the voltage drop averages 3.7 volts. At least 2.3 volts are required to secure any decomposition of sodium chloride in water.

The hydrogen released at the cathode is sometimes made to unite with the chlorine from the anodes, forming hydrochloric acid

Distribution of Sodium Hydroxide in the United States, 1929

Industry	Tons
Soap	103,000
Chemicals	90,000
Petroleum refining	116,000
Rayon	105,000
Lye	25,000
Exports	62,000
Textiles	40,500
Rubber reclaim	40,000
Vegetable oils	11,000
Pulp and paper	37,000
Miscellaneous	33,000
Total	662,500

Bases.—We have already learned that bases are substances that in water solution turn red litmus paper blue and, when added in excess to an acid solution, neutralize the sour taste and all the characteristic properties of acids.

Bases are formed when such metals as sodium, potassium, or calcium react with water.

$$2\ Na + 2\ H_2O \longrightarrow NaOH + H_2,$$
$$Ca + 2\ H_2O \longrightarrow Ca(OH)_2 + H_2.$$

Commercially, however, the most active bases, the so-called alkalies, sodium hydroxide and potassium hydroxide, are made by electrolysis of water solutions of the appropriate metallic chloride. Calcium hydroxide is most cheaply prepared by addition of water to quicklime, CaO.

$$CaO + H_2O \longrightarrow Ca(OH)_2.$$

All the bases contain OH groups attached to a metal. (Some other types of compounds also contain OH groups but not attached to a metal.)

Insoluble Bases.—Most of the metallic hydroxides are insoluble, like ferric hydroxide, $Fe(OH)_3$. They are conveniently prepared by addition of a solution of any one of the alkalies or any soluble bases to a solution of some salt of the metal in question.

$$FeCl_3 + 3\ NaOH \longrightarrow 3\ NaCl + Fe(OH)_3,$$
$$CuSO_4 + 2\ KOH \longrightarrow K_2SO_4 + Cu(OH)_2.$$

Reaction of Bases with Acids.—All bases react with acids to form water and a salt, a process called neutralization.

$$K\boxed{OH + H}Cl \longrightarrow H_2O + KCl,$$

$$Cu\boxed{(OH)_2 + H_2}SO_4 \longrightarrow 2\ H_2O + CuSO_4.$$

EXERCISES

1. What volume of hydrogen at 25° C. and 740 mm. may be liberated from water by the sodium formed by the electrolysis of 1 K. of NaOH?

2. What weight of cupric hydroxide is formed by the interaction of 10 g. of copper sulfate ($CuSO_4 \cdot 5\ H_2O$) with excess of sodium hydroxide in aqueous solution?

3. In a chlorine plant 25 tons of sodium chloride were electrolyzed daily. (*a*) Calculate the weight of sodium hydroxide formed. (*b*) What volume of hydrogen would be liberated?

4. How many grams of sodium hydroxide would be required to form 250 cc. of a molar solution? How many to form 4.5 liters of a normal solution?

5. What weight of sodium hydroxide is needed to neutralize 45 cc. of a 0.5 normal solution of sulfuric acid?

CHAPTER XVI

IONIZATION

Introduction.—In a previous chapter we have said that acids, bases, and salts differ in certain respects from other substances. A brief restatement of their nature may be clarifying.

Acids all contain hydrogen, although not all hydrogen compounds are acids, sugar for example. Acid solutions in water ordinarily taste sour, turn blue litmus red, release carbon dioxide from carbonates, and react with most metals with displacement of hydrogen.

The common bases are compounds of a metal with oxygen and hydrogen. In water solution they turn red litmus blue. Such metallic hydroxides as those of sodium, potassium, and calcium ($NaOH$, KOH, $Ca(OH)_2$) have already been mentioned.

A salt is formed by the reaction between an acid and a base, the other product being water. Salts may be formed in several other ways.

$$NaOH + HCl \longrightarrow NaCl + H_2O,$$
$$Ba(OH)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2\ H_2O.$$

Here the sodium chloride and barium sulfate are salts.

Evidences of Ionization.—The examples of *double decomposition* already studied exhibit an exchange of groups or radicals when acids, bases, or salts are mixed in aqueous solution:

$$Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2\ NaCl,$$
$$H_2SO_4 + Ba(NO_3)_2 \longrightarrow BaSO_4 + 2\ HNO_3.$$

In these two equations we observe a tendency for the sulfate radical ($—SO_4$) to break away from sodium or hydrogen and unite with barium. Before the sulfate group can unite with barium there must be a dissociation of sodium sulfate and also of barium chloride. The easy and instant exchange of the same radicals in such reactions leads us to suspect a preliminary decomposition of acids, bases, and salts into radicals as soon as dissolved in water. So the name "double decomposition" is appropriate. In displacement we have a similar separation into radicals:

$$Zn + H_2SO_4 \longrightarrow H_2 + ZnSO_4.$$

One of the most convincing pieces of evidence of such dissociation in water is found in the ***abnormally large values for freezing point lowering, boiling point rise, and osmotic pressure of aqueous solutions of acids, bases, and salts.*** A solution of a gram molecular weight of sugar, glycerine, etc., in 1000 g. of water freezes at − 1.86°. It makes no difference whether heavy sugar molecules or light alcohol molecules are dissolved, the only consideration is *number of dissolved particles.* Doubling the concentration doubles the freezing point lowering. After observing this it is astonishing to learn that a solution containing one gram molecular weight of sodium chloride per 1000 g. of water freezes at a temperature approaching *twice* 1.86° below zero. Since this solution apparently contains exactly the same number of molecules as the sugar solution (a gram molecular weight of each taken) and since the only influence on freezing point lowering is *number* of dissolved particles, we are forced to the only possible conclusion, namely that some of the sodium chloride molecules must have broken down, dissociated into smaller particles, thus accounting for more particles than the original number of molecules. Now there is only one way for such a simple compound to dissociate, for there are only two atoms in each molecule of sodium chloride:

$$NaCl \longrightarrow Na + Cl.$$

Obviously, if all the salt molecules split into two parts, the original number of molecules would be doubled and the solution would freeze at exactly 2 × 1.86° below zero. This complete dissociation is approximated only in very dilute solutions. Evidently the less water present the less the dissociation and with no water (dry salt) only molecules are found.

The student at once admits the necessity of accounting for more particles than indicated by a gram molecular weight and admits that this explanation accounts for them, but he doesn't see how ordinary sodium can exist in contact with water. For that matter he is skeptical about the presence of ordinary chlorine in salt water. Chlorine water is greenish yellow, poisonous, and a powerful oxidizing agent, and he knows by experience that salt water has none of these properties. He remembers that metallic sodium reacts violently with water, but there is nothing exciting to be seen when salt is dissolved in water.

The answer to these doubts is found in the facts of electrolysis, but before discussing that topic there are a few more facts to consider at this point.

A solution containing one gram molecular weight of sulfuric acid has a freezing point lowering approaching three times 1.86°. The inference is that each molecule dissociates into three parts, probably as follows:

$$H_2SO_4 \longrightarrow H + H + SO_4.$$

The sulfate group does not disintegrate, for the freezing point of a solution of copper sulfate ($CuSO_4$) indicates the formation of only two parts per molecule, one of course being copper and the other the sulfate group. In all these dissociations the same radicals form as those taking part in double decomposition, a very significant point.

After all, this conception of dissociation is not without precedent. When ammonium chloride is heated to about 350° and 22.4 liters of its vapor weighed, we find the data indicate a much smaller molecular weight than corresponds to the formula NH_4Cl. Fortunately, there are simple tests which show a dissociation of the hot molecules:

$$NH_4Cl \longrightarrow NH_3 + HCl.$$

This behavior of ammonium chloride once made chemists question Avogadro's hypothesis.

The fraction dissociated can be calculated from the freezing point of the solution. Suppose one tenth of a gram molecular weight of sodium chloride (5.85 g. NaCl) were dissolved in 1000 cc. of water and the solution froze at $-\ 0.356°$. If no molecules dissociated, the freezing point lowering of this 0.1 molar solution would have been 0.186° $\left(\frac{1.86°}{10}\right)$, so the *excess lowering* produced by extra particles beyond the ordinary molecules must be 0.356° less 0.186°, or 0.170°. Therefore $\left(\frac{0.170}{0.186}\right)$, or 91.4 per cent of the molecules, were dissociated.

$$8.6 \text{ per cent, } NaCl \rightleftarrows (Na) + (Cl), 91.4 \text{ per cent.}$$

This calculation, however, applies only to the ionization yielding two ions per molecule as a limiting possibility, in which case there can be formed at the most only one extra particle per molecule. With sulfuric acid, for instance, three ions per molecule may be imagined as a limiting possibility. Since this suggests the formation of two extra particles for each molecule ionized, the excess lowering should be divided by two, as a preliminary to the calculation of the fraction ionized. The result will really represent the average of two steps of ionization, first the separation of one hydrogen particle and then the separation of the second hydrogen particle.

Exactly the same proof of the dissociation of acids, bases, and salts in aqueous solution can be found in their abnormally great boiling point rise and osmotic pressure.

Exercise 1.—Give this proof for boiling point rise.

Electrolysis.—Although water was decomposed by the electric current as early as 1800 (Nicholson and Carlisle), most of our knowledge of electrolysis, and its terms, we owe to Faraday, the great English chemist and physicist.

When two metallic plates (electrodes) are placed in a solution and connected with a source of current we have an electrolytic cell. If a lamp is placed in the circuit, as in Fig. 67, we can observe by its glow when current is passing. An ammeter measures current more accurately. Place the electrodes in pure water and connect with the ordinary lighting circuit. The failure of the lamp to glow shows that little or no current passes. Evidently water is a poor conductor. Now add sugar or glycerine or alcohol to the water and stir. Even these solutions do not conduct the current. But add dilute sulfuric acid or some soluble salt or base and the lamp glows. In fact any acid, base, or salt dissolved in the water of the cell described will conduct the current. The remarkable fact is that *only acids, bases, and salts* (which we therefore call *electrolytes* or *ionogens*) will do this; all other substances are called nonelectrolytes.

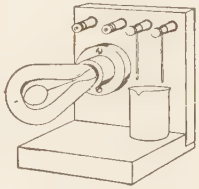


Fig. 67.—The glowing of the lamp shows the passage of an electric current through a solution.

Suppose in the cell of Fig. 68 we use a solution of hydrochloric acid and pass a direct current through the circuit. The "current of electricity" is merely the passage of a stream of electrons along a conductor, solid or liquid. Unfortunately the direction of flow was wrongly indicated before we understood anything about a stream of electrons. The electrode where the current enters, or electrons leave, is called the ***anode*** and the one by which it leaves, or electrons enter, the ***cathode.*** Ions attracted to the anode are called ***anions*** while those attracted to the cathode are termed ***cations.*** The passage of the current merely keeps the anode positively charged and the cathode negatively charged. Hydrogen escapes at the cathode and chlorine at the anode. In other words, hydrochloric acid is electrolyzed. Hydrogen particles from the entire solution travel to the cathode and are there released. Why, unless they are attracted? The cathode is a negatively charged strip of metal and consequently attracts oppositely charged bodies. The conclusion is that the hydrogen particle is simply an atom carrying a positive charge of electricity. In this form it is soluble in water. On contact with the negative electrode its charge is neutralized and the plain hydrogen atoms then unite in pairs to form ordinary hydrogen gas molecules, which escape. The chlorine particles move from all parts of the solution to the anode, or positive electrode. This attraction must be due to the presence of a negative charge on the chlorine particle or atom. On contact with the electrode the charge on the chlorine atom is neutralized and common chlorine escapes and may be detected by the usual tests. Both the hydrogen and chlorine are *primary products of electrolysis.*

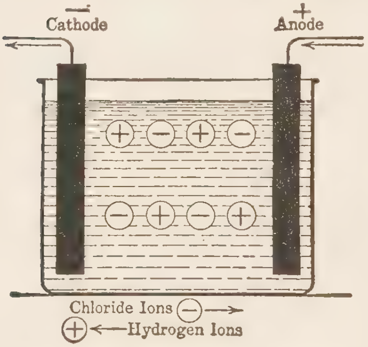


FIG. 68.—Electrolysis of hydrochloric acid.

When sulfuric acid is electrolyzed, its hydrogen is liberated at the negative electrode, as with all acids, but the sulfate radical is not found as a molecular substance at the positive electrode. Instead, oxygen escapes. If the experiment is performed in a U-tube, it can be shown that sulfuric acid accumulates around the positive electrode and diminishes in concentration around the other electrode. Evidently the sulfate radical is attracted by the positive electrode because of the negative charge carried by the radical. After discharge the simple radical, unable to exist in molecular form, reacts with water:

$$2\ SO_4 + 2\ H_2O \longrightarrow 2\ H_2SO_4 + O_2.$$

Of course this sulfuric acid of the equation, a *secondary product of electrolysis*, is itself electrolyzed, and so on indefinitely.

Copper sulfate is electrolyzed with a red deposit of metallic copper on the cathode and escape of oxygen at the anode. Potassium iodide, on electrolysis, shows the color of iodine at the anode and yields the usual blue with a drop of starch paste. At the cathode hydrogen escapes, and if a drop of colorless phenolphthalein solution is added a splendid pink color develops, indicating the formation of a base. Potassium hydroxide is the only one possible. The positively charged potassium atom, after attraction to the cathode and discharge there, inevitably reacts with water as in the following equation:

$$2\ K + 2\ H_2O \longrightarrow H_2 + 2\ KOH.$$

Silver nitrate, on electrolysis, yields a deposit of metallic silver on the cathode (a primary product) while oxygen and nitric acid are formed at the anode (secondary products). Evidently the silver nitrate dissociates into Ag and NO_3 radicals. On discharge at the positive pole the NO_3 radical reacts with water:

$$4\ NO_3 + 2\ H_2O \longrightarrow O_2 + 4\ HNO_3.$$

There is another explanation of the formation of secondary products of electrolysis, and in fairness to the student it should be presented. By this view sulfate ions are not actually discharged, because it is easier to discharge the hydroxyl ions always present (to a very slight extent) in water. These OH-ions after discharge unite in pairs to form water and oxygen, which escapes, leaving the SO_4^- paired off in solution around the cathode, with an equivalent number of H^+ ions from the water. In other words, sulfuric acid accumulates at the anode.

Similarly, by this theory, it is easier to discharge H^+ ions of water at the cathode than to discharge the Na^+ ions. Therefore the Na^+ ions pair off around the cathode with an equivalent number of OH^- ions coming from the water. In other words, sodium hydroxide accumulates at the cathode.

In answer to this theory, held by so many chemists, it may be stated that with very weak currents of electricity and in dilute solutions this explanation may apply, but when larger currents are passed in more concentrated solutions, there are not enough H^+ ions and OH^- ions from the incredibly minute ionization of water to carry the current. Then Na^+ ions, K^+ ions, SO_4^{--} ions, NO_3^- ions, etc., may actually be discharged. Subsequent reaction with water yields NaOH, KOH, H_2SO_4, HNO_3, etc.

Iron ions may be discharged at the cathode from a weakly acid solution, yet hydrogen ions are easier to discharge than the iron ions.

It is an interesting fact that discharge of ions is influenced somewhat by the nature of the electrode. For example, a silver anode goes into solution with formation of Ag^+ ions more readily than NO_3^- ions (or even OH^- ions, for that matter) are discharged on a silver anode. This principle is used in the commercial purification of crude copper. Platinum anodes have practically no tendency to ionize, so NO_3^{--} ions (or, if you prefer, OH^- ions) are discharged on platinum anodes.

When mercury is made the cathode in electrolysis of a solution of sodium chloride, the mercury is found to contain metallic sodium. Evidently in this instance Na^+ ions are discharged in spite of the presence of H^+ ions in the water.

An interesting confirmation of the ionic theory is to be noted in the fact that there is a direct quantitative relation between the conductivity of a solution and the extent of ionization as indicated by the abnormally large values for freezing point lowering, boiling point rise, and osmotic pressure.

From these facts of electrolysis, and others, the Swedish chemist, Arrhenius, deduced his great theory of electrolytic dissociation. In launching this theory Van't Hoff, the Dutch chemist, and Ostwald, the German chemist, aided materially.

The Ionic Theory.— ***Acids, bases, and salts in aqueous solution dissociate into atoms or groups of atoms which carry charges of electricity.***

This explains the possibility of the existence of sodium particles without the expected action on water. A sodium atom carrying a positive charge of electricity is called an *ion;* it is soluble in water, invisible, and does not react with water. Similarly a chlorine atom carrying a negative charge of electricity is called an ion and is a very different substance from greenish-yellow, poisonous chlorine. It is colorless, soluble in water, and non-poisonous. A solution of copper sulfate is blue because of the copper ion. When such a solution is electrolyzed the soluble, positively charged, blue ion is discharged at the negative electrode and becomes common red, insoluble, metallic copper. Truly an electric charge makes a vast difference. A sulfate radical ($—SO_4$) is incapable of separate existence except when loaded with negative electricity.

There is no excess of either positive or negative electricity on the ions dissociating from each molecule of an electrolyte. That is, there must be an equal number of positive and negative charges on the anions and cations.

How else can we explain the *electroneutrality of solutions?* The salty ocean is neither positive nor negative, otherwise there would be very little ocean bathing. If we allow one positive charge to a hydrogen ion (H^+), then there must be one negative charge to a chloride ion (Cl^-) and the ionization of hydrogen chloride is

$$HCl \longrightarrow H^+ + Cl^-.$$

It follows then that in the ionization of sodium chloride the sodium ion must carry one positive charge to equal that on the chloride ion. A series of equations follows, each a logical development from the preceding (except the fourth):

$$\begin{aligned}
&(1) & NaCl &\longrightarrow Na^+ + Cl^-,\\
&(2) & CuCl_2 &\longrightarrow Cu^{++} + Cl^- + Cl^-,\\
&(3) & CuSO_4 &\longrightarrow Cu^{++} + SO_4^{--},\\
&(4) & HNO_3 &\longrightarrow H^+ + NO_3^-,\\
&(5) & AgNO_3 &\longrightarrow Ag^+ + NO_3^-,\\
&(6) & Fe(NO_3)_3 &\longrightarrow Fe^{+++} + NO_3^- + NO_3^- + NO_3^-.
\end{aligned}$$

Faraday's Law.[1]—Faraday gave us an experimental basis for ascribing a definite number of charges to each ion. He found that when a gram equivalent weight of any metal or hydrogen has been liberated from a compound by electrolysis, exactly 96,500 coulombs of electricity have passed through the solution.

Faraday's laws of electrolysis (1833–34) are fundamental.

First Law: ***The mass of any substance liberated at an electrode during electrolysis is proportional to the quantity of electricity passed through the electrolytic cell.***

Second Law: ***When the same quantity of electricity passes through different electrolytes, the masses of the substances liberated at the electrodes are proportional to their chemical equivalents.***

For example, this same quantity of electricity can set free from electrolyte solutions gram equivalent weights of H (1.008 g.), of Ag (107.88 g.), of Cu $\left(\frac{63.57}{2}\text{ g.}\right)$, and of Al $\left(\frac{27}{3}\text{ g.}\right)$. Of course equivalent quantities of the negative ions are being discharged at the same time in electrolysis. That is, one gram equivalent weight of hydrogen chloride is decomposed by 96,500 coulombs of electricity, for this means that one gram equivalent weight of hydrogen and one gram equivalent weight of chlorine are released simultaneously.

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[1] The coulomb is the unit of quantity of electricity, as the liter is a unit of quantity of water.

Electrolysis is merely an attraction and discharge of ions, so there must be 96,500 coulombs of electricity on each gram atomic weight of hydrogen ions or of silver ions. But this quantity of electricity discharges only half of one gram atomic weight of copper $\left(\frac{63.57}{2}\text{g. Cu}\right)$ so there must be $2 \times 96{,}500$ coulombs on a whole gram atomic weight of copper and, by similar logic, $3 \times 96{,}500$ coulombs on a whole gram atomic weight of aluminum. In other words, this 96,500 coulombs is the unit charge. In the case of hydrogen ion it is represented by H^+. For others it is

$$Na^+, K^+, Ag^+, Cu^{++}, Al^{+++}, Cl^-, NO_3^-, SO_4^{--}, PO_4^{---}, \text{etc.}$$

Exercise 2.—Explain how a spoon is silver plated.

Exercise 3.—How many coulombs of electricity are required to decompose 45 g. of copper sulfate?

Exercise 4.—This number of charges on the ion exactly parallels valence. The valence of the phosphate radical (PO_4) is three. How many negative charges does it carry?

Ionization occurs *before* any electric current is turned on so the source of these great charges is a matter of question to the student. We now have convincing evidence that a neutral atom is composed of an equal number of positive and negative charges of electricity. When sodium reacts with chlorine the sodium atom loses one negative charge to the chlorine atom. This loss of one electron leaves the sodium atom with an excess of one positive charge. This reminds us of the relative enrichment of a debtor when some friend assumes a dollar debt for him. Suppose the debtor owned $40 and was also in debt $40. His actual wealth is nothing, but after his friend assumes a one-dollar debt the debtor is really worth one dollar, his financial status is + 1. These negative charges are called ***electrons,*** so we speak of atoms gaining or losing ***electrons.***

In a molecule of sodium chloride the charged atoms are held together by electrostatic forces. Water merely separates the charged atoms, which then become ions.

The essential feature of the reaction between sodium and chlorine is the passage of an electron from the Na atom to the Cl atom. Many chemists now consider it a matter for secondary importance whether the ions thus formed remain firmly bound to one another or are freely movable.

A positive ion is, evidently, a free atom or radical that has lost one or more electrons. A negative ion is a free atom or group of atoms that has gained electrons. Even gaseous molecules are ionized (as shown by the conducting qualities of a flame) by the effect of heat as well as of X-rays, ultra-violet light, and cathode rays in knocking electrons out of gas molecules.

Ionization Equilibrium.—Another annoying question in the mind of the student is this: if oppositively charged ions exist in the same solution, free to move, why do they not attract and discharge each other? They do. But as fast as they unite to form new molecules some other molecules ionize and we merely have a condition of ionic equilibrium which can be disturbed like any other equilibrium:

$$NaCl \rightleftarrows Na^+ + Cl^-.$$

This method of writing the equation shows that there are both molecules and ions present. In more dilute solutions the percentage of molecules ionized is greater. This is reasonable, for dilution keeps the ions farther apart, but has no effect on the action of molecules in breaking apart. At about 0.001 N nearly all salts are almost completely ionized, in fact 0.1 N hydrochloric acid is 93 per cent ionized. Solutions of electrolytes when diluted (up to a certain limit) conduct electricity better than when more concentrated. This is to be expected, for it is the ions that carry the current. For each electrolyte in solution there is a definite concentration that contains the greatest number of these conducting ions per cubic centimeter. ***The passage of electricity along a wire*** is sometimes likened to the flow of water in a pipe, but ***is really a stream of electrons.*** Through solutions electricity is carried by separate moving ions as water is carried in buckets.

The equilibrium in any ionization varies with the electrolyte. Some acids and bases ionize but little. In alcohol there is much less ionization than in water, while in carbon disulfide and benzene there is practically none. Hydrogen chloride dissolves in toluene, but such a solution has no acid properties whatever and does not conduct electricity.

The velocity of migration of ions when attracted to the electrodes is not very great. At 18° under a potential difference of one volt with electrodes one centimeter apart the swiftest ion of all, H^+, moves only 10.8 cm. per hour, OH^- moves 5.6 cm. per hour, Cu^{++} 1.6 cm., K^+ 2.05 cm., and Cl^- 2.12 cm. This migration may be observed by electrolyzing the blue solution of copper sulfate in a U-tube. It is best to have a layer of a colorless electrolyte such as potassium nitrate in the upper part of each arm. The blue of the copper ion slowly moves to the cathode and away from the anode.

The Electron Transfer Explanation of Electrolysis.—In the electrolysis of a water solution of HCl the H^+ ion is attracted to the cathode and there accepts one electron from that cathode, thus becoming neutral hydrogen, insoluble in water. At the same time one electron is given to the anode by a Cl^- which then becomes neutral chlorine. The electrons are carried through the solution by the negative ions, given up at the anode, and passed along the metallic circuit to be presented to positive ions at the cathode. This is electrolysis.

Ionization of Fused Salts.—The high conductivity of molten NaCl and other salts shows beyond question that these molten salts are highly ionized. In fact, the commercial manufacture of metallic sodium, magnesium, aluminum and some other products depends absolutely upon the fused salt ionization. In a solid crystal of NaCl, for example, a single Na atom is bound equally to all its neighboring Cl atoms, not to one alone, as in a molecule (p. 66). These attractions are considered to be due to electric charges on the atoms. Therefore the solid crystal may be said to be ionized even before melting although there is but little freedom of movement on the part of the ions.

In a liquid the same situation holds to a far less degree, and the arrangement is random and always changing. There is, even in liquids, a certain restraint on freedom of ionic movement.

Fused mercuric chloride dissolves many salts to form good conducting solutions. Also in a molten lead salt displacements similar to those in water solutions are known.

$$\text{Fe} + \text{Pb salt} \longrightarrow \text{Pb} + \text{Fe salt.}$$

The Debye-Hückel Theory of Complete Ionization.—On page 66 it was shown that in crystals of salts the molecule as a unit no longer exists, but that rows and planes of atoms or radicals characterize the solid structure. The atoms are already charged, ionized, and are held together by electrical attraction. Debye and Hückel now offer the theory, incomplete as yet, that when the strong electrolytes are dissolved in water in dilutions greater than 0.01 N the molecules are practically completely ionized (as in the solid crystals).

In more concentrated solutions the attracting and repelling forces between ions (closer together than in dilute solutions) as well as the actual volume of the ions, introduces complications. Perhaps reaction between ions and solvent is fundamental to the question. The well-known "neutral salt effect" on the ionization of acids, producing an apparent greater degree of acid ionization, is well illustrated when the rate of inversion of a sugar solution by a weak acid is measured before and after addition of such a neutral salt as sodium chloride. Of course, the dissolved salt produces some change in the association of the solvent molecules. Certainly the activity of the H^+ ion is changed.

It is to be noted that the new theory is still in the making, showing its weakness when applied to concentrations greater than 0.01 N. It denies the existence of HCl molecules in water solution despite the fact that HCl molecules escape from the surface of concentrated solutions. There are many things that this fails to explain, as yet.

Summary.—1. Acids, bases, and salts are the only substances that exchange radicals as in double decomposition, and these same radicals are separated from aqueous solution by electrolysis.

2. Acids, bases, and salts lower the freezing point, raise the boiling point, and produce osmotic pressure in water to an extent not accounted for by the number of molecules. The abnormality of these values is paralleled quantitatively by the electrical conductivity of such solutions. Therefore some of these molecules dissociate (ionize) into additional particles, which produce the abnormal values.

3. Solutions of acids, bases, and salts are the only substances that conduct electricity with resulting decomposition. Solid metals conduct without decomposition.

4. Electrolysis is preceded by ionization and is merely an attraction of radicals to charged plates and release at these plates.

5. The ionic theory explains electrolysis by describing the dissociation radicals of electrolytes (or ionogens) as atoms or groups of atoms carrying electric charges. The cations with positive charges are attracted to the negative plate or cathode and there discharged, while the anions are attracted to the positive anode and discharged. The discharged radicals are released as primary products of electrolysis or react with the water to form secondary products.

6. By Faraday's law equal quantities of electricity liberate equivalent quantities of the ions. A gram equivalent weight of any element or radical carries 96,500 coulombs of electricity and therefore this amount is required to discharge and liberate it.

7. The number of positive and negative charges on the ions from each molecule is equal, as shown by the fact that electrolyte solutions as a whole

show no trace of electrification. The number of charges on an ion is the same as its valence.

8. The source of the charges on the ions is the transfer of electrons (negative charges of about 1/1845 the mass of the hydrogen atom) from the metallic radicals to the non-metallic ones.

9. Ions continually attract, meet, and discharge ions of opposite charge to form molecules, which in turn are continually ionizing. An equilibrium between molecules, and ions exists, depending on the particular electrolyte used, the dilution, the solvent, and temperature

NH_4Cl

EXERCISES

5. If ammonium chloride, when vaporized, completely dissociates into ammonia and hydrogen chloride, what will 22.4 liters of this vapor weigh?

6. Give a convincing array of evidence for the ionic theory.

7. Distinguish between copper and the copper (cupric) ion.

8. State Faraday's law and give an illustration.

9. What does the electroneutrality of solutions of acids, bases, and salts prove?

10. If we had no ionic theory, what would the speed of double decomposition lead you to suspect?

11. A toluene solution of HCl gas does not conduct electricity. Would you expect it to attack zinc or marble ($CaCO_3$) as does a water solution of HCl?

12. Twenty-five grams of sodium nitrate are dissolved in 1000 g. of water. The degree of ionization of the salt in the solution is 70 per cent. What is the freezing point?

13. Twenty g. of barium chloride are dissolved in 1000 g. of water. The degree of ionization is 77 per cent. What is the freezing point?

14. Ten g. of sodium sulfate are dissolved in 600 g. of water. The boiling point of the solution at 760 mm. is 100.15°. What is the degree of ionization?

15. The same current is passed through separate solutions of each of the following compounds: $AgNO_3$, $Pb(NO_3)_2$, $CuSO_4$, $AlCl_3$. Calculate the relative weights of each of the metals present that are liberated.

16. Suppose that, in the previous problem, 1200 coulombs of electricity were passed through each solution. Calculate the actual weight of each metal liberated.

17. What weight of iron would be required to displace from solution the copper in 112 g. of $CuSO_4$?

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CHAPTER XVII

APPLICATIONS OF THE IONIC THEORY

Conductivity and Ionization.—The ability of a solution to conduct electricity (its conductivity) depends upon the number of ions present, the number of electric charges carried by each, and the velocity of ionic migration (see page 210 for comparative velocities). There is a striking parallel between the conductivity, freezing point lowering, and chemical activity of normal solutions of acetic, sulfuric, and hydrochloric acids. As Cady states it, under similar conditions (surface, temperature, etc.) normal acetic acid releases 1 cc. of hydrogen when in contact with zinc in exactly the same time that the zinc discharges 65 cc. of hydrogen from normal sulfuric acid and 100 cc. from normal hydrochloric acid. Under these conditions hydrochloric acid is a hundred times as active as acetic. A normal solution of hydrochloric acid freezes at nearly twice 1.86° below zero, while a normal solution of acetic acid freezes at only a trifle below − 1.86°. Normal acetic acid has but little more effect on freezing point lowering than has sugar. Normal hydrochloric acid conducts electricity well, sulfuric acid about two thirds as well, while normal acetic is only a very poor conductor.

The conclusion from these facts is that hydrochloric acid in normal solution ionizes very well, most of the molecules dissociate, while in normal acetic acid a very small fraction of the molecules have dissociated.

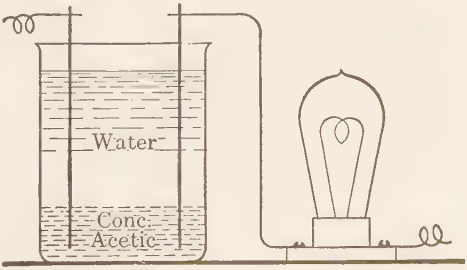


FIG. 69.—Increase of ionization with dilution.

At greater dilutions even acetic ionizes to a greater degree. The molecular conductivity of any electrolyte increases with dilution up to a maximum and then remains the same. This means that finally all the molecules yield conducting ions. For example, the molecular conductivity of hydrochloric acid at 18° is 379 when diluted beyond $\frac{N}{2000}$; this is the maximum and corresponds to complete ionization. At $\frac{N}{10}$ this acid has a conductivity of 351. Evidently $\frac{351}{379}$ or 93% of the molecules have ionized at this concentration. This is a valuable method of measuring the fraction ionized.

In a battery jar (Fig. 69) place two long metal strips as electrodes and fill three-fourths full with water. With a long-stemmed dropping funnel introduce concentrated acetic acid under the lighter water so that there is almost no mixing. After placing a lamp in the circuit turn on the current. The lamp scarcely glows. Now stir the solutions, thus greatly diluting the acid. The bright glowing of the lamp shows the formation of many more ions at the greater dilutions. It is only ions that conduct in solutions.

The Fraction Ionized.—A table giving the percentage of ionization of several acids, bases, and salts is invaluable as a picture of their relative activity. In a general way this property depends on the degree of ionization.

FRACTION IONIZED IN 0.1 N SOLUTIONS AT 18°

ACIDS			BASES		
HCl		0.92	KOH		0.91
HBr	N/2	.90	$NaOH$		.91
HNO_3		.92	$Ba(OH)_2$		.81
$HMnO_4$ Permanganic	N/2	.92	NH_4OH		.013
$H_2SO_4 \rightarrow H^+ + H^+ + SO_4^{--}$		.61	$N(CH_3)_4OH$	N/16	.96
$H \cdot C_2H_3O_2$, Acetic		.0134	H_2O		.000,0001
$H_2CO_3 \rightarrow H^+ + HCO_3^{--}$		.0017			
$H_2S \rightarrow H^+ + HS^-$		.0007			
HCN, Prussic		.0001			
$H \cdot H_2BO_3$, Boric		.0001			
H_2O		.000,0001			

SALTS				
KCl	0.86	K_2SO_4		0.72
$NaCl$	.85	$MgSO_4$		.45
NH_4Cl	.85	$ZnSO_4$		.41
$BaCl_2$	.76	$CuSO_4$		.40
$CaCl_2$	.76	$NaC_2H_3O_2$		.79
KBr	.86	$Cd(NO_3)_2$		.56
$NaNO_3$	.83	$CdBr_2$	N	.16
KNO_3	.82	$HgCl_2$	N	.01
$Sr(NO_3)_2$	.72	$Hg(CN)_2$		A trace
$AgNO_3$	.81			

From this table we learn that "strong" acids, such as hydrochloric and nitric, are 92 per cent ionized in 0.1 N solution. In fact it is this high percentage of ionization that makes them so active chemically or "strong." Sulfuric acid is only moderately strong with 61 per cent ionized. Concentrated sulfuric acid is more destructive to animal and plant tissue, but only 1 per cent of ordinary 95 per cent sulfuric acid is ionized. In such concentrated form it has certain dehydrating and oxidizing properties not observed in the dilute form, but as an acid its activity is less. Acetic acid (found in vinegar) is "weak" with only 1.3 per cent ionized. Carbonic acid is very weak, as we might have known since it is present in the lungs and mouth. Prussic acid is a powerful poison, but as an acid it is still weaker than carbonic. Hydrogen sulfide (H_2S) is an offensive gas, but its water solution is only very faintly acidic.

The common bases, sodium and potassium hydroxide, are the strongest. Calcium hydroxide is not included, because it is not soluble to the extent of 0.1 N solution. In 0.015 N solution it is 90 per cent ionized. Ammonium hydroxide seems strong enough to the nose, but it is really a weak base, only 1.3 per cent being ionized. However, when the four hydrogens are replaced by the organic group, methyl (CH_3), it becomes one of the strongest bases known. The name of this substituted ammonium hydroxide is formidable, tetramethylammonium hydroxide, $N(CH_3)_4OH$, but it means something to the organic chemist.

Salts, with three or four exceptions, are all "strong," or highly ionized in dilute solution. The cadmium halides and some mercuric salts are almost in a separate class.

Acids containing more than one ionizable hydrogen atom to the molecule, such as sulfuric, carbonic, or phosphoric, ionize by stages with increasing dilution. With a certain amount of water a given weight of sulfuric acid may first ionize thus:

$$H_2SO_4 \rightleftarrows H^+ + HSO_4^-.$$

Addition of more water makes it possible for the second hydrogen to ionize. The algebraic balance of positive and negative charges is still correct:

$$HSO_4^- \rightleftarrows H^+ + SO_4^{--}.$$

With carbonic acid (H_2CO_3) there is almost none of the second hydrogen ionized. Phosphoric acid (H_3PO_4) throws off the first hydrogen easily, the second to a very limited degree, and the third almost not at all.

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^-,$$
$$H_2PO_4^- \rightleftarrows H^+ + HPO_4^{--},$$
$$HPO_4^{--} \rightleftarrows H^+ + PO_4^{---}.$$

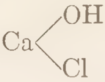
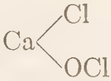
The primary ionization of H_3PO_4 is about 50,000 times the secondary, and this in turn about 500,000 times the tertiary. The primary ionization of H_2SO_4 is only about 33 times the secondary. (Stieglitz.)

There is a possibility of some confusion as to the amount of ionizable hydrogen in 0.1 N solutions of a strong acid and a weak acid. Hydrochloric acid attacks zinc about one hundred times as fast as does acetic, but give the acetic time enough and the same weights of hydrogen will be released by equal volumes of 0.1 N acids. The reason is that ionization is a case of equilibrium:

$$98.7\%\ H\cdot C_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-,\ 1.3\%.$$

If zinc displaces these hydrogen ions from solution, the equilibrium is continuously disturbed to the right (there can be no reversing to the left with hydrogen ions gone) and finally all the acetic acid molecules have ionized. Thus equal volumes of the same normality of all acids contain exactly equal weights of "potential" hydrogen ions, but the strong acids contain much more of "actual" hydrogen ions at any instant than do the weaker acids.

Types of Electrolytes.—It is now clear that an ***acid*** is any substance that, in water solution, yields hydrogen ions. So it is hydrogen ion, common to all acids, that is responsible for the sour taste, the attack on bases, carbonates, and the reddening of litmus. Monobasic acids yield only one hydrogen ion per molecule, as HCl, HNO_3, $H\cdot C_2H_3O_2$, and HCN. Dibasic acids yield two hydrogen ions per molecule, as H_2SO_4. Obviously H_3PO_4 is a tribasic acid. From the formula of acetic acid ($C_2H_4O_2$) it might be thought that four hydrogen atoms should ionize. Only one breaks off as an ion even at great dilutions. The other three are attached differently inside the molecule and are not even potential ions. So we often write the formula $H\cdot C_2H_3O_2$ or even H·acetate.

A ***base*** is any substance that yields hydroxyl ions in water solution. A monacid base yields but one hydroxyl ion per molecule, as KOH, NaOH, and NH_4OH. But $Ca(OH)_2$ is a diacid base and $Al(OH)_3$ a triacid base. We admit that it is only in neutralization that all three hydroxyl groups of $Al(OH)_3$ could be made to ionize, but they are potential ions. ***Salts*** we defined previously as one of the products of the neutralization of an acid by a base, the other being water. They may also be defined as the product of the union of any positive ion, except H^+ ion, with any negative ion except OH^- ion. Normal salts are formed by replacing all the ionizable hydrogen of an acid by a metal, as in Na_2SO_4 or K_3PO_4. Acid salts are formed by replacing only part of the ionizable hydrogen of acids by a metal, as in $KHSO_4$ or Na_2HPO_4. Basic salts result when only part of the hydroxyl groups of a base are neutralized by an acid, as in  $Ca\begin{matrix}\diagup OH\\ \diagdown Cl\end{matrix}$. Mixed salts have, in a single molecule, different metals, as $NaKSO_4$, or different negative radicals, as bleaching powder,  $Ca\begin{matrix}\diagup Cl\\ \diagdown OCl\end{matrix}$.

The positive ion is nearly always a metal with a few such exceptions as hydrogen and the ammonium ion (NH_4^+). The negative ion never contains a metal alone.

Of course we can form any salt by the simple device of mixing the oppositely charged ions. For example, to form barium sulfate we need only take a solution of ***any barium salt*** (because these will furnish Ba^{++}) and mix it with ***any soluble sulfate*** (because these furnish SO_4^{--}). It is a matter of comparative indifference what the other ions accompanying these are. Mix $BaCl_2$ and Na_2SO_4. Solutions of these are already ionized, so we mix four kinds of ions:

$$Ba^{++} + Cl^- + Cl^- + Na^+ + Na^+ + SO_4^{--} \longrightarrow$$
$$BaSO_4 + Na^+ + Na^+ + Cl^- + Cl^-.$$

The student at once asks why $BaSO_4$ was written as a molecule on the right. It is so insoluble that it precipitates, leaving the ions of sodium chloride in solution. So the effect is practically this:

$$Ba^{++} + SO_4^{--} \longrightarrow BaSO_4.$$

Were barium sulfate soluble we should have only its ions in solution in equilibrium with the others and on evaporating we should have a mixture of four salts.

Colors of Solutions.—Water solutions of sodium chloride are colorless at every concentration, so we conclude that sodium ion and chloride ion, as well as the molecules of sodium chloride, are colorless. The sulfate ion must be colorless because sulfuric acid solutions have no color. Copper ion must be blue since dilute solutions of copper sulfate are blue. It may be objected that the blue color is due to molecules. This can't be true, however, because the dry salt, heated until all water is lost, is white yet only molecules remain. In some solutions each ion and the molecules as well may have color. The actual color then is the resultant of a mixture of colors.

If to dry cupric bromide ($CuBr_2$) a very little water is added, the color is brown. With a little more water the color is green and with still more blue. Now the cupric ion is blue (all dilute copper salt solutions are blue) and the bromide ion is colorless (see any solution of potassium bromide), so a very dilute solution of cupric bromide is blue since practically all the brown molecules have dissociated into blue cupric ions and colorless bromide ions. With less water there must be a concentration containing many brown molecules and many blue ions as well. Such a mixture of colors appears green.

The ionization equilibrium can be disturbed in either direction.

$$CuBr_2 \rightleftharpoons Cu^{++} + Br^- + Br^-.$$

To the green solution add solid potassium bromide. This increase in the number of bromide ions gives more opportunities for contact with cupric ions and the reaction to the left is hastened. This increase in formation of brown cupric bromide molecules and decrease in number of blue cupric ions causes the green solution to turn brown. The equilibrium is disturbed to the right when the bromide ions are precipitated by addition of any soluble powdered lead salt to the brown solution. This decreases the number of brown molecules of cupric bromide and increases the number of blue cupric ions. The resulting color mixture is green.

Exercise 1.—To what is the color of a yellow solution of potassium chromate (K_2CrO_4) due? The purple of potassium permanganate ($KMnO_4$) in dilute solution?

Ionogen Reactions.—There are four types of double decomposition:

1. Double decomposition with both products soluble,
2. Double decomposition with one product insoluble,
3. Double decomposition with both products insoluble,
4. Double decomposition with one product only slightly ionized.

As an illustration of (1) we give this:

$$NaNO_3 + KCl \rightleftarrows NaCl + KNO_3,$$
$$Na^+ + NO_3^- + K^+ + Cl^- \rightleftarrows Na^+ + Cl^- + K^+ + NO_3^-.$$

Now any positive ion must inevitably attract, meet, and discharge any negative ion in a solution, so four different equilibrium reactions can be written:

$$\begin{tikzcd}
NaNO_3 \arrow[r, shift left] & Na^+ \arrow[l, shift left] & + & NO_3^- \\
KCl \arrow[r, shift left] & Cl^- \arrow[l, shift left] \arrow[d, shift right] & + & K^+ \arrow[d, shift right] \\
 & NaCl \arrow[u, shift right] & & KNO_3. \arrow[u, shift right]
\end{tikzcd}$$

None of the products remain in the molecular form to any considerable extent in dilute solution, so there is a general balance with most of the material in the form of the four ions.

Type (2) is illustrated by a mixture of solutions of silver nitrate and potassium chloride:

$$\begin{tikzcd}
AgNO_3 \arrow[r, shift left] & Ag^+ \arrow[l, shift left] & + & NO_3^- \\
KCl \arrow[r, shift left] & Cl^- \arrow[l, shift left] \arrow[d] & + & K^+ \arrow[d, shift right] \\
 & AgCl & & KNO_3. \arrow[u, shift right]
\end{tikzcd}$$

Since silver chloride is insoluble both the silver ions and chloride ions are largely removed from solution and tied up in molecules of silver chloride. This steadily aids the ionization of silver nitrate by disturbing the equilibrium to the right. All the silver nitrate ionizes. Similarly with the potassium chloride. Nothing is left but the precipitate and the ions from potassium nitrate (with a few molecules).

Type (3) is not so common. It is illustrated by the reaction between solutions of barium sulfide and zinc sulfate. All the ions concerned are nearly completely removed in the two insoluble products, barium sulfate and zinc sulfide.

$$BaS + ZnSO_4 \longrightarrow BaSO_4 + ZnS.$$

EXERCISE 2.—By this method write the equilibria in a mixture of barium chloride and sodium sulfate.

Type (4) is well represented by neutralization of an acid by a base. Here the hydroxyl and hydrogen ions are tied up in molecules of water, which ionize only to a trifling extent. Equilibria are disturbed to the right and all the acid and base used up.

$$\begin{tikzcd}[row sep=small, column sep=tiny]
NaOH \arrow[r, phantom, "\rightleftharpoons"] & Na^+ & + & OH^- \\
HCl \arrow[r, phantom, "\rightleftharpoons"] & Cl^- \arrow[d, shift right] & + & H^+ \arrow[d] \\
& NaCl \arrow[u, shift right] & & H_2O.
\end{tikzcd}$$

Neutralization.[1]—When a liter of a normal solution of *any strong acid* neutralizes a liter of a normal solution of *any strong base* approximately 13,700 calories of heat are released. Remember, these electrolytes are ionized before mixing.

$$Na^+ + OH^- + H^+ + Cl^- \longrightarrow Na^+ + Cl^- + H_2O + 13{,}700 \text{ cal.}$$

$$K^+ + OH^- + H^+ + Cl^- \longrightarrow K^+ + Cl^- + H_2O + 13{,}700 \text{ cal.}$$

$$2\,Na^+ + 2\,OH^- + 2\,H^+ + SO_4^{--} \longrightarrow 2\,Na^+ + SO_4^{--} + 2\,H_2O + 27{,}400 \text{ cal.}$$

$$Na^+ + OH^- + H^+ + NO_3^- \longrightarrow Na^+ + NO_3^- + H_2O + 13{,}700 \text{ cal.}$$

$$Ba^{++} + 2\,OH^- + 2\,H^+ + 2\,Cl^- \longrightarrow Ba^{++} + 2\,Cl^- + 2\,H_2O + 27{,}400 \text{ cal.}$$

The only thing common to all these reactions is the formation of water. The heat of neutralization is really the heat of formation of 18 g. of water in each case. If sodium chloride really formed and stayed formed in the first reaction above, its heat of formation would be added to 13,700 cal. The same is true for the other salts mentioned, each with a different heat of formation. But the constant value of the heat of neutralization is convincing evidence that the only ions that stay together to any extent are hydrogen and hydroxyl in the form of water. So the essential feature of neutralization is the union of the hydrogen ion of an acid with the hydroxyl ion of a base to form water. Nothing else happens.

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[1] In a normal solution of sodium chloride there are some un-ionized molecules, so the heat liberated must be somewhat more than 13,700 cal.

With reactions between weak acids and bases the heat of neutralization is influenced by the completion of the process of ionization. The weak acids and bases are poorly ionized but the salts formed are well ionized. This brings in the effect of the heat of hydration of ions, for ions do attach to themselves molecules of water. For example:

$$2\,HCl + Zn(OH)_2 \rightarrow ZnCl_2 + 2H_2O + 19{,}880 \text{ cal.}$$
$$HCl + NH_4OH \rightarrow NH_4Cl + H_2O + 12{,}270 \text{ cal.}$$

If, in a conductivity apparatus such as Fig. 69, equal layers of 0.1 N HCl and 0.1 N NaOH are placed with negligible mixing, the lamp glows brightly. No wonder with the fastest ions known, H^+ and OH^-, to carry most of the current. The slower Na^+ and Cl^- also help. On stirring the two layers the swift H^+ and OH^- meet, neutralize each other, and are removed from solution. The slower Na^+ and Cl^- are all that are left to carry the current. It might be expected that since half the ions are gone only half as much current could be carried, but it is worse than that. H^+ and OH^- carried more than half the current because of their greater velocity. Even more striking is the addition of 0.1 N H_2SO_4 to 0.1 N NaOH because when mixed in equivalent amounts practically no current flows. The $BaSO_4$ formed is extremely insoluble and yields almost no ions as compared to NaCl.

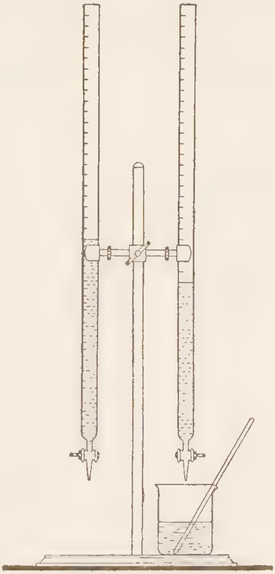

FIG. 70.—Titration.

Titration with Standard Solutions.—A solution of any definite, known concentration is often called a *standard solution.* A normal solution of any acid is such a standard solution and contains 1.008 g. of ionizable hydrogen per liter Since a normal solution of any base contains 17.008 g. ionizable hydroxyl per liter, it is evident that a liter of one exactly neutralizes a liter of the other:

$$H^+ \text{ (1.008 g.)} + OH^- \text{ (17.008 g.)} \longrightarrow H_2O \text{ (18.016 g.)}.$$

In fact equal volumes are equivalent; so if we wished to determine the strength of an unknown solution of sodium hydroxide (or any base) and had, for example, a 0.1 N solution of hydrochloric acid, we could do this by titration. With an accurately marked pipette or burette (Fig. 70) we measure out a convenient volume, say 20 cc., of the acid into a small beaker. A few drops of litmus solution are added to this, turning red, of course. Then we carefully run in (drops, not a stream) the unknown base until one more drop just turns the red to blue. This means that there is just enough base to react exactly with the acid. Suppose 20 cc. of 0.1 N HCl neutralized 16 cc. of unknown sodium hydroxide. It is evident that the volumes of acid and base used must be inversely proportional to their normality. For example, 100 cc. of N acid would neutralize 50 cc. of 2 N base. In this particular case the proportion may be expressed as follows:

cc. acid		cc. base		normality of base		normality of acid
20	:	16	=	x	·	0.1
		$16\,x$	=	2.0		
		x	=	0.125		

Therefore the base is 0.125 N.

If desired, titration problems may be solved in a different way. In the illustration given on this page the number of grams of HCl in 20 cc. of 0.1 N solution could be calculated. Next the number of grams of NaOH required to neutralize this weight of acid could be calculated (equation, etc.). This is, of course, the weight of NaOH actually contained in 16 cc. of the unknown solution, the volume found by the titration experiment to be equivalent to 20 cc. of 0.1 N acid. It is, then, a simple step to compute the weight of NaOH in 1 cc. and in 1 liter.

Such analysis of acid or base solutions is called ***acidimetry*** or ***alkalimetry.*** The color change at neutrality is called the ***end-point*** and the process is ***titration.***

EXERCISE 3.—How many cc. of 0.1 N HCl are required to neutralize 80 cc. of 0.5 N KOH?

EXERCISE 4.—If 44 cc. of unknown sulfuric acid neutralize 30 cc. of N KOH, how many grams of acid are contained in 1000 cc.? What is its normality?

EXERCISE 5.—Remembering that ammonium hydroxide in 0.1 N concentration is only 1.3 per cent ionized, while 0.1 N nitric acid is 93 per cent ionized, would you say that a liter of 0.1 N NH_4OH would just exactly be neutralized by a liter of 0.1 N HNO_3? Explain.

Indicators.—Indicators are substances that change color when solutions pass from the acidic to the basic condition or vice versa. Litmus changes from red in acid to blue in base; phenolphthalein from colorless in acid to purple in base; methyl orange from pink in acid to yellow in base. The sharp color change should indicate neutrality, when the number of H^+ ions exactly equals the number of OH^- ions. but some indicators do not change color until there is a considerable excess of either H^+ ions of OH^- ions. For example, there must be eighty times as many OH^- ions as H^+ ions before phenolphthalein changes to purple. Methyl orange does not become an unmistakable pink until there are a million times as many H^+ ions as OH^- ions. Litmus is more accurate than either.

Hydrolysis.—Hydrolysis is a double decomposition between water and some other compound. Usually the term is applied to a reaction of water with a salt, and yet phosphorus tribromide, which is not a salt, is completely decomposed by water. So is calcium carbide in the formation of acetylene. Water solutions of sodium carbonate are basic. The minute ionization of water (proved by the slight but distinct conductivity of the purest water) is a vital factor.

$$\begin{tikzcd}[row sep=small, column sep=tiny]
\mathrm{Na_2CO_3} & \rightleftarrows & 2\,\mathrm{Na^+} & + & \mathrm{CO_3^{--}} \\
2\,\mathrm{H_2O} & \rightleftarrows & 2\,\mathrm{OH^-} \arrow[d, shift right] & + & 2\,\mathrm{H^+} \arrow[d] \\
 & & 2\,\mathrm{NaOH} \arrow[u, shift right] & & \mathrm{H_2CO_3.}
\end{tikzcd}$$

Only one water molecule out of many millions is ionized, but as the few H^+ ions are tied up in molecules of the very weak carbonic acid (H_2CO_3), every equilibrium is disturbed continuously. Of course formation of the strongly ionized sodium hydroxide does not tie up the OH^- ions. More water ionizes and the excess of free OH^- ions increases until the solution is very strongly alkaline. In reality the carbonic acid ionizes to a greater degree than will account for all this effect:

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^-.$$

But the bicarbonate ion, HCO_3^-, is ionized into H^+ ion and CO_3^{--} ion to such an extremely minute degree that it very effectually removes H^+ ions from the solution.

That $NaHCO_3$ and not H_2CO_3 is formed by the hydrolysis of Na_2CO_3 is evident, for boiling would remove carbon dioxide if the unstable carbonic acid were present, thus disturbing the equilibrium and leaving only sodium hydroxide. Such a product is not obtained on evaporation. The bicarbonate ion (HCO_3^-) is stable.

Solutions of ferric chloride react acidic:

$$\begin{tikzcd}
FeCl_3 \rightleftarrows & Fe^{+++} + & 3\ Cl^- \\
3\ H_2O \rightleftarrows & 3\ OH^- + \arrow[d] & 3\ H^+ \arrow[d, shift right] \\
 & Fe(OH)_3 & 3\ HCl. \arrow[u, shift right]
\end{tikzcd}$$

Ferric hydroxide is insoluble, so it removes OH^- ions from solution and continuously disturbs the ionization equilibrium of water. The other product, hydrochloric acid, ionizes freely and does not remove H^+ ions. So a distinct excess of H^+ ions develops. Acid salts are acid in solution for a different reason as indicated by

$$KHSO_4 \rightleftarrows H^+ + K^+ + SO_4^{--}.$$

Solutions of sodium chloride are neutral, as neither H^+ ions nor OH^- ions are removed from solution:

$$\begin{tikzcd}
NaCl \rightleftarrows & Na^+ + & Cl^- \\
H_2O \rightleftarrows & OH^- + \arrow[d, shift right] & H^+ \arrow[d, shift right] \\
 & NaOH \arrow[u, shift right] & HCl. \arrow[u, shift right]
\end{tikzcd}$$

Both products, sodium hydroxide and hydrochloric acid, ionize freely. There is, then, no excess of either H^+ ion or OH^- ion.

From these type reactions we learn that a salt of a strong base and a weak acid ($2\ NaOH + H_2CO_3 \longrightarrow Na_2CO_3 + H_2O$) is hydrolyzed to a basic solution. Salts of a weak base and a strong acid ($Fe(OH)_3 + 3\ HCl \longrightarrow FeCl_3 + 3\ H_2O$) react acidic in water. Salts of a strong acid and a strong base ($HCl + NaOH$

$\longrightarrow NaCl + H_2O$) react neutral in water. The greater the difference in strength of the acid and base forming a salt the more the salt is hydrolyzed.

Exercise 6.—Diagram the hydrolysis of potassium acetate. Of sodium sulfate.

Hydrolysis is really the reverse of neutralization:

$$\begin{array}{ccc} Fe(OH)_3 + 3\,HCl & \rightleftarrows & FeCl_3 + 3\,H_2O. \\ \text{Neutralization} \longrightarrow & & \longleftarrow \text{Hydrolysis} \end{array}$$

Pure liquid solvents are dissociated to a slight degree into ions, but the conductivity (and hence the degree of dissociation) is extremely small. The specific conductivity of the purest water at 18° is 0.04 times 10^{-6}; of pure liquefied HCl (not the usual water solution) at $-100°$ about 0.2 times 10^{-6}; while a normal water solution of KCl has a conductivity of about 0.1 (without the 10^{-6}) at 18°.

The Electromotive or Displacement Series.—We have already studied the order of activity of metals. Since taking up our study of ionization we see a new meaning in the series. A strip of zinc in dilute sulfuric acid displaces hydrogen. But a strip of zinc in a solution of copper sulfate displaces metallic copper in a manner quite similar except that molecular hydrogen escapes as a gas, while molecular copper deposits as a red powder:

$$Zn + H^+ + H^+ + SO_4^{--} \longrightarrow H_2 + Zn^{++} + SO_4^{--},$$
$$Zn + Cu^{++} + SO_4^{--} \longrightarrow Cu + Zn^{++} + SO_4^{--}.$$

What really happens is that the zinc atom gives two electrons to two hydrogen ions and thus becomes the positive zinc ion. Hydrogen ions with addition of electrons become neutral atoms. They cannot continue an independent existence, so they escape from solution as ordinary hydrogen (H_2). Similarly the zinc atom gives two electrons to the copper ion which without its charge is no longer blue and soluble but red and insoluble. The solution itself changes from a blue solution of copper sulfate to a colorless solution of zinc sulfate. Evidently the zinc atom is better able to throw off electrons than is hydrogen or copper. The whole electromotive series really lists the elements in the order of their ability to take on ionic charges (thus going into solution).

Now it is clear why absolutely anhydrous metallic sodium does not react with cold 100 per cent sulfuric acid. Without water there are no hydrogen ions to rob of their charges.

Ionic Reactions in Liquid Phosgene.[1]—Our theories of solution and ionization have developed largely from a study of water solutions. Yet we have long known that fused salts are excellent solvents for other salts and that they ionize and may be electrolyzed.

Franklin and others called attention to the solution, ionization, neutralization, and electrolysis possible in liquefied ammonia (NH_3, not NH_4OH) as decidedly parallel to similar properties in the usual water system. Others have shown similar parallels in liquefied hydrogen bromide, hydrogen sulfide, hydrogen cyanide, etc.

A. F. O. Germann has added to this list of parent solvents for ionic reactions by a detailed study of liquid phosgene, $COCl_2$ (made by the union of CO and Cl_2). The ease with which solutions of aluminum chloride in phosgene react with metals, metallic oxides, sulfides, carbonates, etc., however, let him to believe that these reactions were of the ionic type, and that the solutions contained ions and would therefore conduct electricity. The experiment verified the prediction, and conductivity measurements have shown that, while phosgene itself is a very poor conductor, the specific conductivity of the solution of aluminum chloride in phosgene increases with the concentration until the more concentrated solutions conduct nearly 100,000 times as well.

It has been shown, then, that phosgene is a weakly ionizing solvent and that when the solution of aluminum chloride in phosgene is electrolyzed, carbon monoxide and chlorine are evolved.

From these and many other observations it seems that anhydrous $AlCl_3$ dissolved in $COCl_2$ reacts to form an acid (in this system), a phosgenate of aluminum chloride, $2\ AlCl_3 \cdot COCl_2$ or $COAl_2Cl_8$ as may be prepared.

$$\left\{\begin{array}{l} SO_3 + H_2O \rightarrow SO_3 \cdot H_2O\ (H_2SO_4),\text{ an acid} \\ 2\ AlCl_3 + COCl_2 \rightarrow 2\ AlCl_3 \cdot COCl_2\ \ (COAl_2Cl_8),\text{ an acid} \end{array}\right.$$

$$\begin{array}{l}\text{Metals dis-} \\ \text{place } H_2 \text{ or } CO\end{array} \left\{\begin{array}{l} H_2SO_4 + 2\ Na \rightarrow Na_2SO_4 + H_2 \\ H \cdot NH_2 + 2\ Na \rightarrow 2\ NaNH_2 + H_2 \\ COAl_2Cl_8 + Ca \rightarrow CaAl_2Cl_8 + CO \end{array}\right.$$

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[1] (Optional.)

Neutralization yields a salt and H_2O or NH_3 or $COCl_2$	HCl +	$NaOH \rightarrow$	$NaCl$ +	H_2O, the solvent
	$2\ NaNH_2$ +	$H_2CN_2 \rightarrow$	Na_2CN_2 +	$2\ NH_3$
	the base	the acid →	the salt	the solvent
	$COAl_2Cl_8$ +	$CaCl_2 \rightarrow$	$CaAl_2Cl_8$ +	$COCl_2$
	the acid	the base	the salt	the solvent

The parallel reactions of neutralization are interesting because in each case the product formed in addition to a "salt" is the same as the solvent used, H_2O or NH_3 or $COCl_2$. Similar systems should conform to the implied rule.

When water (a poor conductor) is electrolyzed after addition of a little H_2SO_4 or Na_2SO_4 to make it conducting the solvent is decomposed ($H_2O \longrightarrow H_2 + O$). So it is in the phosgene system —the products of electrolysis are CO and Cl_2.

Acids in water and in liquid ammonia yield H^+ ions but in phosgene acids are substances that yield CO^{++} ions. Carbon monoxide is the product displaced by metals rather than hydrogen as in the other systems.

In the water system bases yield OH^- ions, capable of reacting with the acidic H^+ ions to form more of the solvent, H_2O. In the ammonia system KNH_2 for example, is a base, yielding NH_2^- ions which react with acidic H^+ ions to form more of the solvent, NH_3.

In the phosgene system a base is a substance such as $CaCl_2$, which in solution yields Cl_2^{--} ions (the same ions the pure solvent yields to a very limited extent).

Salts in any system are formed when the anion of the acid unites with the cation of the base.

$$SO_4^{--} + 2\ K^+ \longrightarrow K_2SO_4,$$
$$Al_2Cl_8^{--} + Ca^{++} \longrightarrow CaAl_2Cl_8.$$

To sum it up we may quote from Germann:[2]

"A parent solvent is the substance from which a system of solvo acids, solvo bases and solvo salts is derived.

"A solvo acid is any electrolyte which, in a given solvent, yields cations identical with the cations of the parent solvent, and anions containing, in addition to the atom characteristic of the individual solvo acid, atoms characteristic of the anion of the parent solvent.

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[2] *J. Am. Chem. Soc.*, *47*, 2464, 1925.

"A solvo base is any electrolyte which, in a given parent solvent, yields simple metal cations, and anions identical with the anions of the parent solvent.

"A solvo salt is the electrolyte produced when a solvo acid reacts with a metal, or with a solvo base derived from the same or other parent solvent."

Brönsted, offering a general theory for all systems, says that "acids and bases are substances capable of splitting off or adding on hydrogen ions."

$$\text{Acid} \rightleftharpoons \text{base} + H^+.$$

The pH Notation.—It is now the custom among biologists and many chemists to express faint degrees of acidity and alkalinity in pH values instead of normalities. By the pH value is meant the logarithm of the number of liters of a solution which must be taken in order to contain one gram-ion of hydrogen (1.008 g. of H^+). There is only 1 gram-ion of hydrogen in 10,000,000 liters of pure water for water is only minutely ionized. Since the log. of 10,000,000 is 7 it is evident the pH value of pure water, or of a neutral solution, is 7. In acid solutions the pH value is less then 7 and in basic solutions more than 7. The pH value of the stomach solution is between 1 and 2.5, due to the presence of hydrochloric acid. The blood, however, is slightly alkaline or basic with a pH value of 7.5.

EXERCISES

7. What is the result of mixing copper with a solution of zinc sulfate? Explain. Explain the action of iron on a solution of copper sulfate.

8. Cupric hydroxide, $Cu(OH)_2$, is a very weak base. Does an aqueous solution of $CuSO_4$ react acidic or basic?

9. How does hydrolysis prove the ionization of water?

10. What is an acid in the ammonia system? In the phosgene system?

11. Compare neutralization in the water, ammonia and phosgene systems.

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CHAPTER XVIII

SULFUR AND HYDROGEN SULFIDE

SULFUR

Sulfur was known to the ancients. The brimstone of the Bible was sulfur. Later the alchemists considered it one of the three fundamental elements.

Occurrence.—Sulfur occurs free in volcanic regions, possibly because of the reaction between sulfur dioxide and hydrogen sulfide found in volcanic gases:

$$2\ H_2S + SO_2 \longrightarrow 2\ H_2O + 3\ S.$$

Sedimentary sulfur also occurs in large deposits because of the reduction of calcium sulfate by bituminous material to form calcium sulfide (CaS), the release of hydrogen sulfide by the action or carbonic acid on the calcium sulfide, and final oxidation of the hydrogen sulfide to free sulfur. Up to 1900 Sicily produced 90 per cent of the world's sulfur, but for several years its production has declined and is now about 250,000 tons per year. About 1904 the production of Louisiana sulfur by the Frasch process made the United States quite independent. Previously we imported about 175,000 tons annually. The United States now produces over 80 per cent of the world's sulfur. We export 850,000 tons from our total production of 2,400,000 tons.

Combined sulfur is very common. Iron pyrites (FeS_2), once called "fool's gold," is found in most of our states and in nearly all countries. In fact some of our most important metals occur combined with sulfur, as lead sulfide or galena (PbS), zinc blende (ZnS), and chalcopyrite ($CuFeS_2$). The sulfates also occur in great quantities. The most common are calcium sulfate or gypsum ($CaSO_4 \cdot 2\ H_2O$), barite ($BaSO_4$), celestite ($SrSO_4$), and Epsom salt ($MgSO_4 \cdot 7\ H_2O$).

Sulfur is an essential element in all protein material and so is found combined in plants and animals. Hence the production of the offensive-smelling hydrogen sulfide on decay. Egg yolk is so rich in combined sulfur that antique eggs are easily recognized by the overpowering odor of hydrogen sulfide.

Preparation.—Sulfur volatilizes at very moderate temperatures and thus is distilled away from its impurities. The vapors are condensed in large brick chambers. At first before the brick walls are heated by the gases, the sulfur settles as a yellow dust called "flowers of sulfur." Later it condenses as a liquid which is cast into sticks of "roll sulfur."

In the United States the clever invention of Herman Frasch, an American chemist, made possible the cheapest production of pure sulfur (99.5 per cent) yet known. In Louisiana and Texas great beds of sulfur occur at depths approaching 900 ft. Borings through the overlying rock reach the bottom of these deposits and through this hole three or four concentric pipes are driven (Fig. 71). The outer pipe has a diameter of about 8 in. Relying on the remarkably low melting point of sulfur (114.5°) water at 170° C. under 100 lbs. pressure is forced down an outer pipe to melt the sulfur. But sulfur is twice as heavy as water, so to make it lighter hot air is forced down the innermost pipe (1 in.) to fill the liquid with bubbles. The frothy mixture rises between the air pipe and the hot water pipe and flows into great wooden bins, where it cools to huge blocks. Many wells yield 500 tons daily. Some of the bins produce a single block containing a few hundred thousand tons of sulfur. The great block is dynamited into fragments, as needed for loading on trains.

Exercise 1.—Why doesn't the dirt come up with the melted sulfur in the Frasch process?

Physical Properties.—Sulfur is a pale-yellow solid, tasteless, and nearly odorless, insoluble in water but soluble in carbon disulfide and some other solvents. It exists in a number of different forms with distinctly different properties. This is an example of ***allotropy.*** Ozone and ordinary oxygen are allotropic forms of the same element. White and red phosphorus are also examples of allotropes. The stable form of sulfur, at ordinary temperatures, crystallizes in the rhombic system, but above 96° it slowly changes into the needle-like monoclinic crystals. On cooling the monoclinic crystals below 96° they change very slowly to rhombic crystals. Thus 96° is a transition point.

Exercise 2.—In what connection have we mentioned transition points before?

There is a distinct change in properties in this transition. The density of rhombic sulfur is 2.06 and its melting point 114.5°. The density of monoclinic sulfur is 1.96 and its melting point 119°.

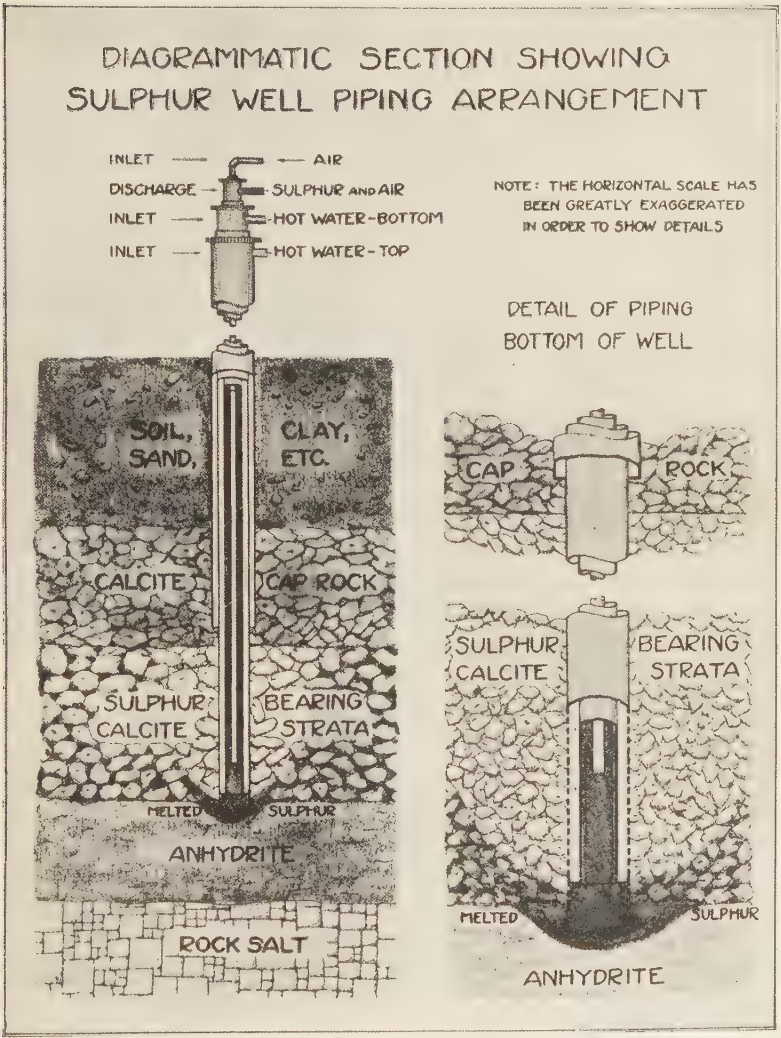
DIAGRAMMATIC SECTION SHOWING
SULPHUR WELL PIPING ARRANGEMENT
INLET
AIR
DISCHARGE
SULPHUR AND AIR
INLET
HOT WATER-BOTTOM
INLET
HOT WATER-TOP
NOTE: THE HORIZONTAL SCALE HAS BEEN GREATLY EXAGGERATED IN ORDER TO SHOW DETAILS
DETAIL OF PIPING
BOTTOM OF WELL
SOIL, SAND,
CLAY, ETC.
CALCITE
CAP ROCK
SULPHUR CALCITE
BEARING STRATA
MELTED
SULPHUR
ANHYDRITE
ROCK SALT
CAP
ROCK
SULPHUR CALCITE
BEARING STRATA
MELTED
SULPHUR
ANHYDRITE

Fig. 71.—Sections of a sulfur well.

Of course natural sulfur is rhombic. This form can be obtained in the laboratory by allowing a solution in carbon disulfide to evaporate slowly (away from flames). If a large mass of molten sulfur (about 200 g.) is cooled slowly, the surface crust punctured, and the liquid below poured out, the dish will be found to contain a mass of needles of monoclinic sulfur. On long standing below 96° these become rhombic. Apparently the needles remain, but upon examination they are found to be made up of minute rhombic crystals.

Amorphous Sulfur.—When sulfur is melted at 114.5° it is a pale-yellow, mobile liquid. At 160° it darkens and becomes very viscous. At 180° the tube can be inverted and the sulfur does not run out. Above this temperature the sulfur again becomes more fluid and boils at 444.7°. Alexander Smith calls the pale-yellow liquid $S\lambda$ and the thick dark liquid $S\mu$. He proved that at intermediate temperatures the two forms are in equilibrium, shifting with the temperature. If sulfur heated nearly to boiling is quickly poured into cold water, it solidifies before crystals have time to form and is a rubbery mass. This soon hardens and then is only partially soluble in carbon disulfide. Crystalline S is removed by this solvent, leaving noncrystalline $S\mu$. A trace of iodine acting as a negative catalyst delays the return of amorphous sulfur to the crystalline form.

Amorphous $S\mu$ is also made by the reaction between sulfur dioxide and hydrogen sulfide, at 0°. (See page 229.) Solutions of polysulfides when acidified yield a suspension of $S\mu$ called ***milk of sulfur.*** The solid removed after slow settling is insoluble in carbon disulfide.

Sulfur Vapor.—At 250° (under low pressure) sulfur must be represented by S_8 since 22.4 liters weigh 256 g. At 800° the G. M. V. weighs 64 g., so S_2 is then the formula. At intermediate temperatures S_6 may exist but probably only mixtures of S_8 and S_2. At 2000° the element is monatomic and S_1 is the formula.

Chemical Properties.—Sulfur is very active when heated. Merely rubbing it in a mortar with mercury produces black mercuric sulfide (HgS). When heated it unites with all metals except gold and platinum and, when the reaction is once started, much heat is evolved. If a tube of sulfur and iron filings is heated to glowing, the glowing continues even after removal from the flame. Moist sulfur is slowly oxidized in the air:

$$2\,S + 2\,H_2O + 3\,O_2 \longrightarrow 2\,H_2SO_4.$$

It can be oxidized quickly by strong oxidizing agents, such as hot nitric acid. In fact sulfur compounds are torn down by this method and the sulfur converted into sulfuric acid. It may then be converted into insoluble barium sulfate and weighed. This is the basis of our quantitative determination of sulfur in minerals, and in foods. Of course hot sulfur burns in air to form sulfur dioxide—and a trace of trioxide.

Hot sulfur unites with carbon to form carbon disulfide, with hydrogen to form hydrogen sulfide, and with chlorine to form sulfur monochloride (S_2Cl_2). This was once thought to be SCl, hence the misleading name. Here the valence of sulfur is one, but in H_2S it is two, in SO_2 it is four, and in SO_3 it is six.

Uses.—The normal consumption of sulfur in the United States was not more than 500,000 tons until the war shut off importations of iron pyrites. This forced the direct burning of Louisiana-Texas sulfur for production of sulfuric acid. Manufacturers are satisfied with this method because of the great purity of the product so our consumption of sulfur is now over 1,500,000 tons annually, in addition to a huge surplus exported. Large quantities are needed for vulcanizing rubber.

Rubber.—In 1839 Charles Goodyear, an American inventor, discovered that by heating raw rubber with sulfur the elastic strength was greatly increased and that the warm-weather stickiness and cold-weather brittleness disappeared. He also discovered that on "filling" the rubber and sulfur with certain oxides of lead it "vulcanized" or reacted with sulfur in much less time and gained better wearing qualities. Thereby he laid the foundations for a billion-dollar industry.

Rubber occurs in the sap or latex of the rubber tree grown in Brazil and the East Indies. The latex, a milky emulsion of 32 per cent rubber in water with a little protein, is coagulated so that the solids separate from the water by smoking, or by natural souring or by addition of acetic acid. When wild Brazilian rubber was the only source the natives used the first two methods, but now that 95 per cent of the world's 500,000 tons of raw rubber per year is obtained from cultivated plantations in the East Indies the acetic acid method is preferred. The coagulated mass is washed, masticated between rolls, and compounded with sulfur and with fillers, such as zinc oxide and fine gas black (carbon), and with an accelerator to speed up vulcanization. The dough is then molded and heated to about 140° C.

Without accelerators, the vulcanization now possible in a few minutes took three hours or longer.

It is not to be thought that zinc oxide, gas-black carbon, barium sulfate, white lead, and the other fillers are added merely to cheapen the product. They add strength and wearing qualities to a high degree. A tire made of pure rubber and sulfur would not run a thousand miles. The smaller the particle of a filler the better. We know that rubber is $C_{10}H_{16}$, but the chemistry of vulcanization is still far from clear.

We have become so accustomed to the uses of rubber that we lose sight of the marvel of it all. "It is used for certain purposes because it is elastic, for others because it is air-tight and water-tight, for others because it is a non-conductor of electricity, for others because it is a shock absorber, and for others because it is adhesive." A great engineer says that the application of rubber as packing for the steam engine and connecting machinery has been essential to the development and extended use of steam as a motive power.

Without rubber tires the automobile industry would be an infant industry only. Rubber air-brake hose on trains, rubber shoes, boots and coats, rubber hot-water bottles, rubber-coated balloons, rubber mats, rubber garden hose, rubber belts, bands, golf balls, rubber insulation for wires—these make up a part of our debt to rubber, to sulfur, and to Charles Goodyear.

A possible source of rubber is the Mexican guayule shrub, which contains rubber throughout the wood, unlike the rubber tree, which contains a rubber latex in the bark.

The use of organic accelerators in the vulcanization of rubber (introduced about 1906) has reduced the time required for the proper action of sulfur on rubber to one third what it was in 1902 and greatly improved the quality of the final product. William C. Geer estimates that the saving to the world in time, equipment, and wear is not less than $200,000,000 annually, a great service rendered by Oenslager and others.

Sulfur is used in making sulfur monochloride, which has another outlet besides the rubber industry. It is the foundation of mustard gas, the most effective poison gas. Sulfur is in demand in the manufacture of carbon disulfide and matches and the sulfur black dyes. Free sulfur is a necessary part of black gunpowder and of many fungicides and germicides for plants. Europe annually applies 100,000 tons of the element to vines and hops. The lime-sulfur spray is famous in this country. As a basis for sulfur dioxide it is necessary in bleaching straw and some other fabrics and has been in demand for bleaching dried fruits, English walnuts, etc. Sulfur has a high electric insulating power, resists wetting by water, is inactive towards most acids, and has a fair degree of physical strength. These properties promise the development of new uses.

Exercise 3.—How many grams of sulfur are required to make 45 liters of sulfur dioxide?

Distribution of Sulfur in 1927

United States

	Tons
Heavy chemicals, (H_2SO_4, etc)	490,000
Fertilizer and insecticides	300,000
Pulp and paper	260,000
Miscellaneous	118,000
Explosives	65,000
Dyes and coal tar products	40,000
Rubber	35,000
Electro-chemicals	20,000
Fine chemicals	13,000
Paint and varnish	5,000
Food products	3,000
Petroleum products	1,000
Total Domestic Consumption	1,232,000
Exports	750,000
Total Distribution	2,100,000

Hydrogen Sulfide

Scheele (1777) published the first detailed investigation of its properties, although something was known of hydrogen sulfide before his time. Soon after this it was used in analysis. At the very time that Lavoisier was insisting that all acids contained oxygen it was shown that hydrogen sulfide is not an oxygen acid.

Exercise 4.—How did Lavoisier reconcile the composition of hydrochloric acid with his views on acids?

Hydrogen sulfide is found in some natural waters, such as the so-called "sulfur springs," in volcanic gases and in Mexican oil wells. Since albuminous material contains combined sulfur, its decay in the absence of air produces hydrogen sulfide. Thus sewer gas always contains hydrogen sulfide. In the distillation of soft coal some hydrogen sulfide is formed, necessitating the filtration of the coal gas through layers of ferric oxide.

✓ **Preparation.**—Hydrogen unites with hot sulfur vapor to form hydrogen sulfide. The most convenient laboratory method of preparation is the addition of some nonoxidizing acid to a sulfide, preferably ferrous sulfide (FeS) because it is the cheapest:

$$FeS + 2\ HCl \longrightarrow FeCl_2 + H_2S.$$

This reaction is reversed very slightly, partly because the gas is only moderately soluble and most of it escapes. It might reasonably be expected that iron pyrites (FeS_2) would be better since it is still cheaper, but it is not used because it does not react with an acid to form hydrogen sulfide, unless "active" hydrogen is present.

Soluble sulfides, such as sodium sulfide, react with acid more rapidly (better contact), but for simple regulation of flow as in a Kipp generator the insoluble ferrous sulfide is best.

$$Na_2S + 2\ HCl \longrightarrow 2\ NaCl + H_2S.$$

Since hydrogen sulfide is an acid in aqueous solution, the sulfides of metals are its salts. Many occur in nature and many are formed by addition of soluble sulfides to salt solutions. Any sulfate can be reduced by heating with carbon. If hydrogen sulfide is made from the resulting metallic sulfide, the sulfate can be recognized:

$$BaSO_4 + 2\ C \longrightarrow BaS + 2\ CO_2,$$
$$BaS + 2\ HCl \longrightarrow BaCl_2 + H_2S.$$

✓ **Physical Properties.**—Hydrogen sulfide is a colorless gas, liquefying at − 61.6° and freezing at − 82.9°. Its critical temperature is 100°. At room temperatures about three volumes dissolve in one volume of water. It readily escapes from water. The odor is disgusting. Small amounts in the air may cause headaches and nausea. Air containing 1 part in 200 is fatal if breathed long, and the concentrated gas is quickly fatal. Since this gas is evolved in some manufacturing processes it is an industrial poison. The gas is about one and a fifth times as heavy as air, so it can be collected by air displacement. (Why not over water?)

✓ **Chemical Properties.**—A solution of hydrogen sulfide open to the air soon has a film of sulfur on the surface, showing how easily it is oxidized. A rapid oxidation is secured by burning the gas in air:

$$2\,H_2S + O_2 \longrightarrow 2\,H_2O + 2\,S,$$
$$S + O_2 \longrightarrow SO_2.$$

If a cold dish is held in the middle of the burning jet for a minute, a yellow spot forms. This is sulfur, of course, so it is evident that in the interior of the flame where there is no contact with air the unburned gas has been dissociated by heat. The dish merely condenses the sulfur vapor before it has opportunity to burn (Fig. 72):

$$H_2S \rightleftarrows H_2 + S.$$

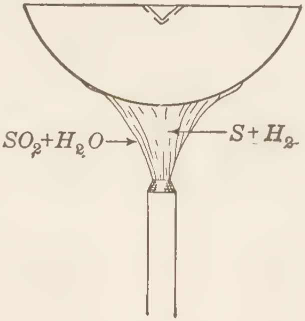

FIG. 72.—Hydrogen sulfide flame cooled by porcelain dish. Yellow sulfur deposits on the dish.

EXERCISE 5.—What are the products when hydrogen sulfide is burned with a large supply of air?

This reaction is reversible, as the two elements are known to unite when heated. The gas cannot be dried by concentrated sulfuric acid because the concentrated acid oxidizes it. Phosphorus pentoxide is a suitable dryer in this case. Oxidizing agents of all kinds attack hydrogen sulfide.

Hydrogen sulfide is an extremely weak acid in water solution. The first hydrogen atom ionizes very little and the second to a minute degree, less than water, in fact.

$$H_2S \rightleftarrows H^+ + HS^-,$$
$$HS^- \rightleftarrows H^+ + S^{--}.$$

One liter of water saturated with hydrogen sulfide at 25° contains, states Engelder,

0.95×10^{-4} gram-ions of H^+,
0.95×10^{-4} " " " HS^-,
1.2×10^{-15} " " " S^{--},
0.1 gram-mole " H_2S.

✓ **Use in Analysis.**—Hydrogen sulfide is invaluable in qualitative analysis and useful in quantitative work also. In a solution of copper sulfate, for example, this gas precipitates black cupric sulfide:

$$CuSO_4 + H_2S \longrightarrow CuS + H_2SO_4.$$

Other sulfides formed in similar ways are black HgS, orange Sb_2S_3, yellow As_2S_3 and CdS, and white ZnS. In the system of qualitative analysis we divide the sulfides into two great groups:

1. Sulfides insoluble in dilute strong acid (CuS, HgS, As_2S_3, etc.).
2. Sulfides insoluble in neutral or alkaline solution but soluble in dilute strong acid (NiS, MnS, ZnS, etc.).

The reason zinc sulfide, for example, is not precipitated in acid solution is that addition of a strong acid like hydrochloric increases greatly the number of H^+ ions present. This gives infinitely more opportunities for contact between the very few S^{--} ions and H^+ ions so more S^{--} ions are removed from the field, tied up as HS^- ions or H_2S molecules. This leaves so few S^{--} ions that the Zn^{++} ions do not form enough zinc sulfide molecules to saturate the solution and thus precipitate.

How different if a strong base is added! The great excess of OH^- ions ties up nearly all the H^+ ions and so the equilibrium is disturbed to the right, producing an enormous increase in number of S^{--} ions.

$$H_2S \rightleftarrows H^+ + H^+ + S^{--}.$$

Now there are enough of S^{--} ions to react with Zn^{++} ions and form more zinc sulfide than the solution will hold. Precipitation occurs. The sulfides of copper and its group are so much more insoluble in water that they can be precipitated in spite of the suppression of ionization of hydrogen sulfide by a strong acid. Ferrous sulfide is so susceptible to the action of acid that it cannot be precipitated by passing hydrogen sulfide into a ferrous salt solution:

$$FeCl_2 + H_2S \rightleftarrows FeS + 2\ HCl.$$

This equilibrium puts nearly everything on the left. The hydrochloric acid formed may be said to dissolve the sulfide. It really suppresses the ionization of the hydrogen sulfide so that the Fe^{++} ions with the S^{--} ions (now in very low concentration) fail to form enough FeS to saturate the solution. But add a base. The acid is neutralized and ferrous sulfide precipitates at once.

There are a few sulfides which are hydrolyzed completely in water, so attempts to precipitate them (in absence of acid) produce hydroxides:

$$Al_2S_3 + 6\ H_2O \longrightarrow 2\ Al(OH)_3 + 3\ H_2S.$$

Sodium, potassium, and ammonium sulfides are soluble and are hydrolyzed considerably.

EXERCISE 6.—How does hydrogen sulfide react with iodine?

EXERCISE 7.—Sodium sulfide (Na_2S) is a salt of $NaOH + H_2S$. Represent graphically its hydrolysis in solution.

When an *excess* of hydrogen sulfide is passed into sodium hydroxide solution, for example, only NaHS is produced. To make Na_2S, an equivalent quantity of sodium hydroxide must be added:

$$NaOH + NaHS \longrightarrow Na_2S + H_2O.$$

This is accomplished quite simply by dividing any solution of the base into two equal parts, saturating one part with hydrogen sulfide and then mixing the two parts.

EXERCISE 8.—Does this suggest a convenient way to make Na_2SO_3 instead of $NaHSO_3$ from SO_2? Or Na_2CO_3 from CO_2? These three gases have a certain resemblance.

Polysulfides.—When sulfur is shaken or warmed with a solution of a sulfide, a polysulfide is formed:

$$Na_2S + S \longrightarrow Na_2S_2.$$

Evaporation produces residues corresponding to formulas ranging from Na_2S_2 to Na_2S_5, depending upon how much sulfur was added. All the persulfides (polysulfides) are unstable, slowly releasing sulfur. This makes them invaluable as insecticides and fungicides. Lime-sulfur wash (CaS_4 or CaS_5) is a famous one. Yellow ammonium sulfide, $(NH_4)_2S_x$, is a reagent in qualitative analysis and is more red than yellow to tell the truth. The bottle labeled $(NH_4)_2S$ should contain a colorless liquid, but this solution always has a yellow tint because of decomposition with release of free sulfur which then adds on to other molecules, forming a little of the colored polysulfide.

If acid is poured into a polysulfide, free sulfur is formed and hydrogen sulfide escapes (write the equation); but if the polysulfide is poured into very dilute acid, a yellow oil separates, probably H_2S_5. (Write the equation for this.)

It is possible that in lime-sulfur sprays the following reaction takes place:

$$3\ Ca(OH)_2 + 12\ S \rightarrow 2\ CaS_5 + CaS_2O_3 + 3\ H_2O.$$

Penthionic acid ($H_2S_5O_6$) is very probably the fungicidal or toxic factor associated with sulfur. When removed (by treatment with ammonia) the the remaining sulfur is non-toxic, but in contact with oxygen and moisture regains its toxicity and again responds to a test for pentathionic acid (p. 255). The oxidation of sulfur probably proceeds as follows:

$$\begin{gathered} S + O_2 \rightarrow SO_2, \\ SO_2 + H_2O \rightleftarrows H_2SO_3, \\ H_2SO_3 + S \rightleftarrows H_2S_2O_3, \\ 5\ H_2S_2O_3 \rightarrow 2\ H_2S_5O_6 + 3\ H_2O. \end{gathered}$$

EXERCISES

9. 100 g. of sulfur heated with copper gave 298.27 g. of copper sulfide (CuS). If you knew only that the atomic weight of sulfur was 32.06 and that the atomic weight of copper was in the neighborhood of 60–70, how would you calculate the exact atomic weight of copper?

10. Why was the Frasch process of getting sulfur out of the ground in Louisiana-Texas a great military asset for the Allies during the war?

11. Why do we produce more sulfur now than we did at the height of the war?

12. Prove that at least a few S^{--} ions are found in a water solution of H_2S.

13. What volume of H_2S at 20° C. and 750 mm. may be produced by the action of HCl on 15 g. of FeS?

14. How many cubic centimeters of H_2S will precipitate the copper in 50 cc. of a N/10 solution of a copper salt?

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CHAPTER XIX

SULFURIC ACID AND THE OXIDES OF SULFUR

In this year's work the student will have little to do with more than sulfur dioxide and trioxide, sulfurous, sulfuric, and thiosulfuric acids.

Sulfur Dioxide

There is nothing new about sulfur dioxide. It was mentioned in Homer's time as a disinfectant; and Paracelsus, the alchemist, knew something of its bleaching powers. Priestley first made it in pure form and recognized it as a definite compound (1775). It occurs in volcanic gases and in some spring waters.

Exercise 1.—What relation has this occurrence to the great sulfur deposits in Italy? (See previous chapter.)

Preparation.—*1. Burning Sulfur.* Sulfur burns in air with a pale blue flame, forming sulfur dioxide. In the United States this is a great commercial source.

$$S + O_2 \longrightarrow SO_2.$$

2. Roasting Sulfide Ores. This is the most common commercial source of sulfur dioxide. Many common metals occur as sulfides which when roasted produce gases dangerous to vegetation and to health. In some states laws forced the smelters to prevent this nuisance. As a result many smelters attached sulfuric acid plants to utilize the waste sulfur dioxide, so everybody profited. The situation is complicated if the smelter is in the Rocky Mountains, so far from sulfuric acid markets that the freight rates are prohibitive. The great copper and zinc smelter at Anaconda, Montana, solved the nuisance problem by building a giant stack over 600 feet high on a hill still higher. Consequently the fumes from the roasting sulfides are mixed with the atmosphere at a height considerably more than 1000 feet above the valley and are carried away by the winds at safe dilutions. This plant utilizes some of the sulfur dioxide and may finally use it all.

The cheapest sulfide ore is iron pyrites (FeS_2), which burns like coal:

$$4\ FeS_2 + 11\ O_2 \longrightarrow 2\ Fe_2O_3 + 8\ SO_2.$$

Zinc sulfide (ZnS) must be fed preheated air:

$$2\ ZnS + 3\ O_2 \longrightarrow 2\ ZnO + 2\ SO_2.$$

Sulfur dioxide from roasting sulfide ores is, of course, diluted with several volumes of nitrogen from the air. For this reason it is suitable only for sulfuric acid manufacture.

3. Reduction of Sulfuric Acid. Hot, concentrated sulfuric acid readily gives one oxygen from each molecule to metals and other reducing agents. In fact under some conditions it has been known to give up all of its oxygen. A very convenient laboratory method of preparation makes use of this principle. Copper scrap is heated with the concentrated acid, but is not made hot enough to boil the acid:

$$\begin{array}{ll} (1) & Cu + H_2SO_4 \longrightarrow CuO + H_2O + SO_2 \\ (2) & CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O \\ \hline (3) & Cu + 2\ H_2SO_4 \longrightarrow CuSO_4 + 2\ H_2O + SO_2. \end{array}$$

We remember from its place in the activity series of metals that copper does not displace hydrogen from acids, so it is clearer to write this reaction in steps. At first the copper is oxidized and then the copper oxide is readily attacked by acid. Equation (3) sums up (1) and (2).

Carbon may be used or even sulfur instead of copper:

$$C + 2\ H_2SO_4 \longrightarrow CO_2 + 2\ SO_2 + 2\ H_2O.$$

EXERCISE 2.—Write the equation for the oxidation of sulfur by sulfuric acid.

4. Acids on Sulfites. A simple laboratory method of preparation is found in the slow dropping of some dilute acid on sulfites. The gas may be dried over anhydrous calcium chloride.

$$Na_2SO_3 + 2\ HCl \longrightarrow 2\ NaCl + H_2O + SO_2.$$

Physical Properties.—Sulfur dioxide is a colorless gas with a peculiar choking odor. It is 2.2 times as heavy as air and is easily liquefied. In fact an ice-salt mixture will liquefy it at ordinary pressures. The liquid boils at $-\ 8°$ and freezes at $-\ 76°$

into a snowlike solid. It is conveniently kept for laboratory use in tin cylinders. Eighty volumes dissolve in one volume of water at 0° and 760 mm.

Chemical Properties.—A water solution of sulfur dioxide reacts weakly acidic and when bases are added sulfites are formed. This indicates a reaction with water. Sulfurous acid and sulfur dioxide are both present in equilibrium:

$$SO_2 + H_2O \rightleftarrows H_2SO_3.$$

It is possible that sulfurous acid appears to be weak because most of it is present as dissolved sulfur dioxide. Compare with the remark on the ionization of ammonium hydroxide (Chap. XXIV). Sulfur dioxide reacts with chlorine to form sulfuryl chloride:

$$SO_2 + Cl_2 \longrightarrow SO_2Cl_2.$$

In addition to its reaction with water, with chlorine, and with hydrogen sulfide, sulfur dioxide unites with oxygen to form sulfur trioxide, a reaction greatly aided by suitable catalysts. In the presence of moisture it is a strong reducing agent and has valuable bleaching properties.

EXERCISE 3.—What is the reaction with hydrogen sulfide?

Uses.—Sulfur dioxide is used to some extent as a refrigerant (because it is volatilized and liquefied at convenient temperatures). Huge quantities are necessary to the manufacture of sulfuric acid and of calcium sulfite for paper making. A great deal is used in bleaching and some in fumigation, although formaldehyde has almost displaced it from that field.

Sulfurous Acid.—As stated in connection with sulfur dioxide, sulfurous acid is formed to a limited extent by reaction of that gas with water. It is a weak acid ionizing in two stages:

$$\begin{aligned}&(1)\ H_2SO_3 \rightleftarrows H^+ + HSO_3^-,\\&(2)\ HSO_3^- \rightleftarrows H^+ + SO_3^{--}.\end{aligned}$$

Reaction (1) proceeds to the right to a slight extent and reaction (2) to a minute extent. Addition of OH^- ions from a strong base disturbs both these equilibria to the right.

In the air this acid slowly adds on oxygen to form sulfuric acid and in general it acts as a strong reducing agent.

Exercise 4.—To remove excess chlorine after a fabric has been bleached with that substance an "antichlor" is added. "Hypo" and sulfurous acid or sulfites are used. Write the equations showing how sulfurous acid in water uses up the free chlorine.

Sulfites.—If an excess of sulfur dioxide is bubbled through a solution of a base such as sodium hydroxide, an acid salt called sodium bisulfite is formed:

$$NaOH + H_2SO_3 \longrightarrow NaHSO_3 + H_2O.$$

This reminds us of the similar reaction of hydrogen sulfide. And just as with that gas, addition of an equivalent amount of the base to the solution of bisulfite forms the normal sulfite:

$$NaOH + NaHSO_3 \longrightarrow Na_2SO_3 + H_2O.$$

Exercise 5.—How does this reaction prove that the HSO_3^- ion dissociates at least slightly into simpler ions?

Calcium bisulfite, $Ca(HSO_3)_2$, is the most important of these salts because of its ability to dissolve the lignin which cements the fibers of cellulose in wood. Chips of soft woods are heated in bisulfite solutions and the cellulose fibers are separated as paper pulp.

Exercise 6.—How is calcium bisulfite made?

Sulfur Trioxide.—Sulfur trioxide is a colorless liquid boiling at 46° and freezing at 15°. It readily ***polymerizes*** (two or more molecules uniting to form larger molecules) especially in the presence of traces of moisture, forming sulfur hexoxide (S_2O_6), a white crystalline mass looking like asbestos. Sulfur trioxide reacts with water to form sulfuric acid. Under sulfur dioxide and sulfuric acid we discuss its formation by the catalytic oxidation of the dioxide.

Sulfuric Acid

Sulfuric acid was much used by the alchemists. Basil Valentine, in the fifteenth century, secured sulfur trioxide and the acid by distilling ferric sulfate and Geber writes of making it from other sulfates in the thirteenth century.

$$Fe_2(SO_4)_3 \longrightarrow Fe_2O_3 + 3\ SO_3,$$
$$H_2O + SO_3 \longrightarrow H_2SO_4.$$

Yet the manufacture of this great acid, the most important compound made by man, was not put on a commercial basis before 1765. Then sulfur and "niter" (KNO_3) were burned together in the presence of air in glass globes. In 1793 the oxidation process was made continuous by the employment of oxides of nitrogen as a catalyst.

Gay-Lussac towers were first used in 1827 to recover the catalytic oxides of nitrogen while the Glover tower was developed in 1859.

The industry is now so enormous that the United States makes over 8,000,000 tons (50° Beaumé) annually. There are two rival processes of manufacture, each especially adapted to certain kinds of raw material and each suited to certain grades of product.

Lead-Chamber Process.—The essential reactions in the huge lead-walled towers and chambers involve the oxidation of sulfur dioxide to the trioxide in the presence of enough water to form sulfuric acid. A mixture of air and the dioxide reacts very slowly, so nitric acid vapors are introduced to oxidize more rapidly:

$$2\ HNO_3 + H_2O + 2\ SO_2 \longrightarrow 2\ H_2SO_4 + NO + NO_2.$$

The cost of nitric acid would make this process economically impossible were it not for the fortunate fact that the nitrogen dioxide (NO_2) released as a by-product is itself capable of oxidizing sulfur dioxide:

$$SO_2 + H_2O + NO_2 \longrightarrow H_2SO_4 + NO.$$

Now another fortunate fact saves the day—and much money. If this nitric oxide (NO), the by-product here, were wasted, the lead-chamber process would soon become historical only. But luckily this nitric oxide has a property—possibly somewhat dry for the student but of thrilling interest to the men owning lead chamber plants—of rapidly uniting with the oxygen of air to form the useful nitrogen dioxide:

$$2\ NO + O_2 \longrightarrow 2\ NO_2.$$

In fact nitric oxide is a catalyst, making the oxygen of air unite with sulfur dioxide in a roundabout way and itself being regenerated time after time. The nitric acid, then, was merely a starter

—a source of the oxides of nitrogen. Most authorities refer to nitrogen trioxide as the catalyst. However at the temperature of the lead chambers this gas dissociates to a very great extent as follows:

$$N_2O_3 \rightleftarrows NO + NO_2.$$

The explanation is quite logical for either gas as catalyst, but it is simpler as given above. There is yet much dispute about these reactions.

As shown in the diagram, Fig. 73, the sulfur dioxide is produced in the burners by roasting some sulfide, usually iron pyrites, in a strong draft of air. However, the modern practice in the United States is to burn sulfur itself in specially designed roasters. Only 20 per cent of our sulfuric acid is now made from pyrites. The pot containing sodium nitrate and concentrated sulfuric acid is heated by the flue gas to distill off nitric acid:

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3.$$

This mixture of flue gases, nitrogen of air, excess oxygen, sulfur dioxide, and the nitric acid vapors, enters the Glover tower. This is a tall tower loosely filled with broken tile, coke, or brick which forces good mixing of the gases with the liquid splashing down from the top of the tower. This liquid supplies the water necessary, so the reactions mentioned now proceed in this tower. Possibly about 16 per cent of the total acid of the plant is formed right in this tower.

The liquid introduced at the top is a compound of oxides of nitrogen with concentrated sulfuric acid. Luckily this compound is decomposed by water with instant release of the oxides of nitrogen, ready for work as catalyst. So a stream of concentrated "nitrosyl" sulfuric acid meets a stream of water (really dilute acid) *inside* the tower. Here a nice economy operates. The released oxides of nitrogen (with those from the action of nitric acid) are swept on by the great stream of other gases into the first chamber. But the diluted acid splashing down the tower meets hot gases fresh from the burners, water is evaporated and passes on into the chambers as steam (where it is needed), and the acid, now cheaply concentrated to 65-78 per cent, is tapped off at the base of the tower. Everything goes just where it is needed, apparently nothing wasted.

The lead chambers, from three to five in number, are huge affairs, often 25 × 30 × 130 feet, each with capacities of about 100,000 cubic feet. They are really inverted boxes suspended so that their lower edges allow the constant overflow of acid collecting on the floor but do not allow escape of gases except by the stack or Gay-Lussac tower. These chambers are lined with sheets of lead melted together at the edges by oxyhydrogen flames. Lead is used because it is not attacked by acid of the concentration produced in the chambers.

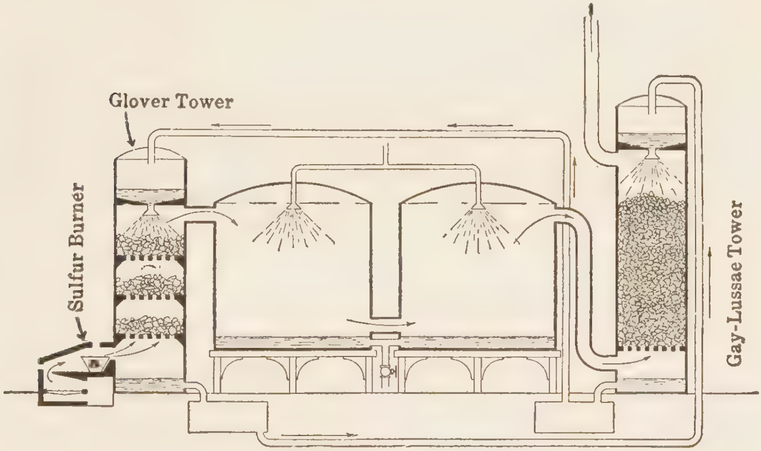
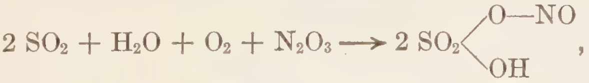
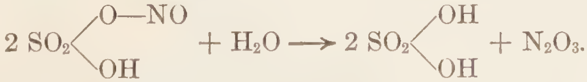


Fig. 73.—Lead chamber process of making sulfuric acid.

The reactions already given express only the general effect of the oxides of nitrogen. It is really somewhat more complicated, and according to Lunge we must imagine the intermediate formation and decomposition of nitrosyl sulfuric acid. He uses nitrogen trioxide in his equations (at chamber temperatures largely a mixture of nitric oxide and nitrogen dioxide).

(1) 

$$2\,SO_2 + H_2O + O_2 + N_2O_3 \longrightarrow 2\,SO_2\begin{cases} O\text{—}NO \\ OH \end{cases},$$

(2) 

$$2\,SO_2\begin{cases} O\text{—}NO \\ OH \end{cases} + H_2O \longrightarrow 2\,SO_2\begin{cases} OH \\ OH \end{cases} + N_2O_3.$$

In equation (1) we have the formation of the nitrosyl sulfuric acid, a white crystalline compound which is not allowed to separate. Enough steam is forced into the chambers to react with it instantly, thus forming sulfuric acid and releasing the catalyst as in equation (2). When the plant is not running properly, these crystals sometimes collect on the lead walls and on decomposing form a little nitric acid, which attacks lead.

A most convincing lecture experiment may be performed to prove the existence of nitrosyl sulfuric acid. In a very dry half-liter flask put not more than three drops of concentrated nitric acid. Pass in a very slow stream of sulfur dioxide gas from a cylinder of the liquid. At first red-brown oxides of nitrogen are seen. Note that there is some water in the nitric acid:

$$H_2O + 2\,SO_2 + N_2O_3 + O_2 \rightarrow 2\,H(NO)SO_4.$$

Now pass in just enough sulfur dioxide to make the red-brown color disappear. A frostwork of white crystals forms over the walls of the flask. These are the "chamber crystals," or nitrosyl sulfuric acid. Add water, drop by drop, to the flask. The crystals disappear with evolution of considerable heat and release of red-brown oxides of nitrogen. Now add about 50 cc. of water and test for sulfates by adding a solution of barium chloride. A white precipitate insoluble in hydrochloric acid proves that sulfuric acid was formed in the experiment.

An excess of steam is used in the chambers for two reasons. First, if the sulfuric acid forming and collecting on the floor were concentrated, it would take up the catalyst, thus stopping the whole process. Second, the lead walls would be attacked by acid of high concentration. So the "chamber acid" is only 62–70 per cent concentration. This corresponds to a specific gravity of 1.5–1.62 and about 60° Be.

To give the gases full opportunity to react a series of from three to five chambers is provided and even then some sulfur dioxide is lost. The great volume of atmospheric nitrogen present forces the use of a chimney or stack, and this is made in the form of the Gay-Lussac tower, resembling the Glover tower. Oxides of nitrogen released at the end of the last chamber would be lost to the air, ruining the process, but for the clever use of the fact that concentrated acid reacts with these oxides, forming a solution of

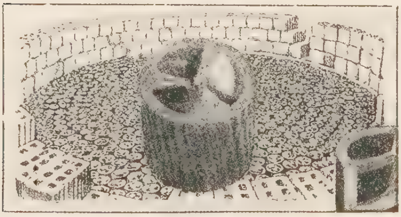


FIG. 74.—Spiral-channel ceramic filling for acid towers and splash towers generally.

nitrosyl sulfuric acid. The concentrated acid splashes down over the broken tile and is forced from the bottom of the Gay-Lussac to the top of the Glover tower (by compressed air), where it releases its oxides of nitrogen as previously described. Unfortunately not all the catalyst is recovered and continuous replacement from nitric acid is necessary. With the two towers only 30 to 40 pounds of sodium nitrate per ton of sulfuric acid are required. Acid from the bottom of each tower is pumped to the top of the other.

In the newer plants the tendency is to build smaller chambers. The Mills-Packard system uses circular towers, cooled externally by water, and fed with a spray of water from the top. In other plants towers with shallow trays of acid force better mixing of gas, or mists and sprays of acid are introduced into the chambers.

The chamber acid is suitable for use in the manufacture of soluble phosphate fertilizer from phosphate rock, but for most other purposes it must be concentrated. Eventually the rival contact process will make all the concentrated acid leaving the demand for 62–70 per cent acid to the chamber process. This is boiled down in lead pans or sprayed down a tower against a rising current of hot flue gases to reach a concentration of about 77 per cent. A compact layer of lead sulfate forms in the pans but protects the lead beneath. Acid above 77 per cent, however, dissolves lead sulfate (hence the presence of a little lead as impurity in commercial acid) and the work must be finished in glass, platinum, or cast iron vessels to a concentration of about 94 per cent and a specific gravity of 1.84. Although iron is readily attacked by dilute acid, it is not affected by the acid of high concentration, just the reverse of the effect on lead. To make C. P. acid the commercial grade is distilled from glass or porcelain, securing a concentration of 98 per cent. The rest is water.

Exercise 7.—Without help make a detailed drawing of the lead-chamber plant, using arrows to show the flow of gases and liquids.

Exercise 8.—Why not use ten chambers since considerable loss of oxides of nitrogen occurs with five chambers?

The Contact Process.—Something was known of the contact process long before, but it was only in 1901 that the German chemist, Knietsch, made it a commercial success. A mixture of sulfur dioxide and air is led through a series of iron tubes containing a porous supporting material such as asbestos or magnesium sulfate which holds the catalyst, finely divided platinum. The most favorable temperature for the platinum catalyst is about 400°. Below this temperature the action is too slow, and above this temperature the equilibrium is displaced in the wrong and costly direction:

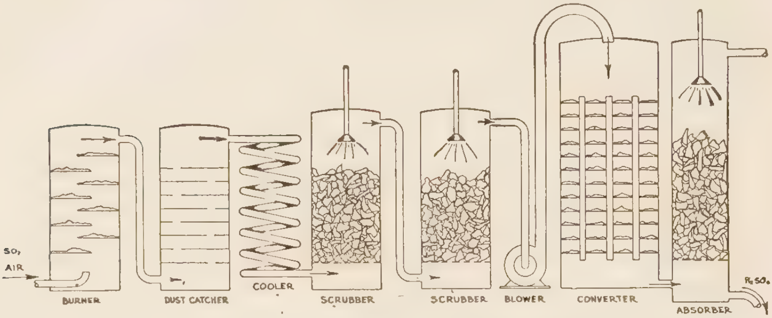


Fig. 75.—The contact process of making sulfuric acid.

$$SO_2 + O \rightleftharpoons SO_3 + 22{,}600 \text{ cal.}$$

Since the reaction desired is exothermic, the catalyst must be cooled somewhat by passing the cold gases around the tubes to hold the temperature to 400° or a little higher. Sulfur trioxide is decomposed to some extent at 500°, completely at 1000°. It is the universal practice to pass the sulfur trioxide into 98 per cent acid, maintaining that concentration by a sufficient stream of water. This seems absurd until we learn that the gas is not readily absorbed by water. In fact, if the acid is more dilute than 98 per cent, enough water vapor from the acid will meet the bubbles of SO_3 to form minute droplets of H_2SO_4. These droplets, like all fogs, become insulated by an adsorbed film of air. Furthermore, the droplets move very slowly as compared with SO_3 molecules, hence smash into the wall of each air bubble with far less frequency. Successful absorption of SO_3, then, depends upon a sufficiently low vapor tension of the acid.

The expensive platinum used as a catalyst (several times as expensive as gold) is easily "poisoned" by impurities in the sulfur dioxide, especially the oxide of arsenic, which is commonly found in the flue gases from iron pyrites and some other sulfides. Great care is taken to wash out all dust. Many very cheap solids catalyze the reaction to some extent and ferric oxide is actually used in a few plants. It gives its best yield (40 per cent conversion into sulfur trioxide) at about 625°. The conversion must then be completed by platinum.

During 1929 compounds or mixtures containing vanadium as one of the catalytic elements came into commercial use in contact sulfuric acid plants. The advantages claimed are low cost of the catalyst and freedom from poisoning. The conversion efficiency is said to be very high when the catalyst functions at about 570°.

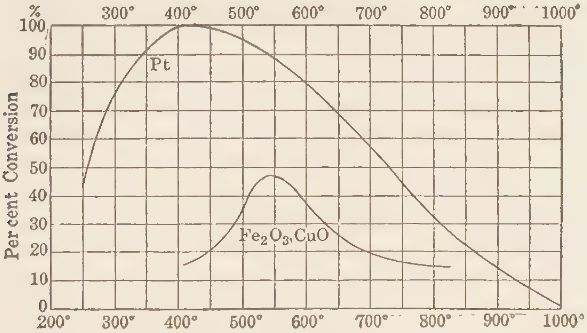


FIG. 76.—Variations in the per cent conversion of SO_2 to SO_3 at different temperatures when catalyzed by platinum (upper curve) or by a mixture of the oxides of iron and copper (lower curve). The best temperature for the usual contact process is just above 400° C., while a higher temperature, about 550°, is required for the cheaper Fe_2O_3, CuO catalyst. (Curves from Knietsch.)

The product of the contact process is very pure and can be made 100 per cent by adding exactly the correct amount of water.

The contact and lead chamber processes supplement each other. For production of acid of very high concentration and purity the contact process will always be cheaper. In fact, oleum, or "fuming" sulfuric acid (100 per cent acid in which much SO_3 is dissolved) can be made only by the contact process. For vigorous action in some industries (notably, the manufacture of explosives), no other acid strength will serve. But for the crude acid of moderate concentration (50° Beaume) suitable for acid treatment of phosphate rock in the fertilizer industry, the lead chamber plant is pecularily adapted. In the United States about one-third of our sulfuric acid is made by the contact process.

One contact plant operated for fifteen years using 400 oz. of platinum to convert 100,000 tons of SO_2.

The usual gas mixture led through the contact mass contains about seven per cent SO_2 (the rest being air). The reaction is highly exothermic, so heat exchangers for warming up the incoming gas are used. Common practice is to divide the catalyst into two parts. Relatively little platinum is used in the first part, for it is easy to secure conversion of 80 per cent of the sulfur dioxide. The greater part of the platinum is used to complete the conversion, operating at a different temperature.

The traditional method of introducing into the lead chamber process catalytic oxides of nitrogen from the action of sulfuric acid on sodium nitrate is rapidly giving way to the newer catalytic oxidation of ammonia as a source of oxides of nitrogen. Small units are attached directly to the chamber plant. A mixture of about ten per cent ammonia gas and 90 per cent air preheated to about 200° C. to 300° C. is passed through platinum gauze maintained at a temperature of about 900° C. There is a considerable saving in costs wherever the ammonia oxidation unit is installed.

Properties of Sulfuric Acid.—Pure anhydrous sulfuric acid is an oily colorless liquid ("oil of vitriol") with a density of 1.838 at 15°. It boils at 338° with some decomposition ($H_2SO_4 \rightleftarrows SO_3 + H_2O$). As the gases cool they combine again, forming droplets of sulfuric acid with the appearance of dense, white fumes. The constant boiling acid is 98.33 per cent concentrated. Decomposition is marked at 100° and complete at 450°.

Sulfuric acid mixes in all proportions with water with the evolution of much heat. To avoid sudden generation of steam and consequent spattering the concentrated acid is always slowly poured into the water (which cools it). The oxidizing power of hot, concentrated acid has already been discussed, also its dehydrating power. It removes hydrogen and oxygen in the proportion to form water from various compounds. Because of its high boiling point it is nearly always used when any more volatile acid is to be released from its salts by heating the mixture:

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3.$$

On heating carefully, the other acid, practically always more volatile, is driven off continuously. Sulfuric is a moderately strong acid (see page 214). With a little water it throws off one

H^+ ion. It is more difficult to throw off the second one, but at greater dilutions this is done:

$$H_2SO_4 \rightleftarrows H^+ + HSO_4^-,$$
$$HSO_4^- \rightleftarrows H^+ + SO_4^{--}.$$

Uses.—The petroleum industry was the first to demand huge quantities of sulfuric acid. Petroleum contains unsaturated compounds that darken by oxidation in air. These are removed by mixing with the concentrated acid. Much chamber acid is used direct by fertilizer factories as a means of converting calcium phosphate rock into soluble acid phosphate. The manufacture of nitroglycerin and smokeless powder calls for a large tonnage, so it is evident that this great acid was indispensable in the recent war, as it is at any time, to make possible mining and excavations for railways. The tremendous importance of the Louisiana and Texas sulfur deposit now becomes apparent. Concentrated sulfuric acid is necessary to the manufacture of hydrochloric acid from salt and of nitric acid from sodium nitrate. It finds considerable demand as a rust remover from sheets of iron or steel to be tinned or galvanized. At present by far the greatest demand for sulfuric acid is in making fertilizers (including the manufacture of ammonium sulfate). Oil refining and chemical manufacture are next in order of demand.

USE OF SULFURIC ACID IN U. S. BY INDUSTRIES (1929)

Fertilizers	2,360,000
Petroleum Refining	1,570,000
Chemicals	820,000
Dyes and Coal Products	820,000
Steel Pickling	770,000
Metallurgical Uses	625,000
Paints, Pigments	215,000
Explosives	195,000
Textiles	85,000
Miscellaneous	320,000
	7,925,000

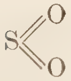
Sulfates.—Many sulfates occur in nature and many are in common use. Gypsum ($CaSO_4 \cdot 2\ H_2O$), when heated with loss of three fourths of its water, becomes plaster of Paris. Mixed with water this powder "sets" to a solid. Hence its use in making plaster casts:

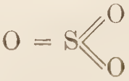
$$2\ CaSO_4 \cdot H_2O + 3\ H_2O \longrightarrow 2\ [CaSO_4 \cdot 2\ H_2O].$$

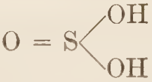
The sulfates are often called "vitriols" (from "oil of vitriol"). Green ferrous sulfate is "green vitriol," etc. All the sulfates are soluble except those of barium, strontium and lead. Calcium sulfate is soluble only to a very limited extent. The alums are double sulfates to be discussed later.

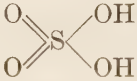
Sulfates are reduced to sulfides when heated with carbon or fused with calcium hydride, CaH_2.

Structure of the Oxides and Acids of Sulfur.—


Sulfur Dioxide


Sulfur Trioxide


Sulfurous Acid


Sulfuric Acid

Other Acids of Sulfur.—When sulfur is boiled with a solution of a sulfite it adds on directly, forming a salt of *thiosulfuric acid.* The free acid is unstable:

$$Na_2SO_3 + S \longrightarrow Na_2S_2O_3,$$
$$Na_2S_2O_3 + 2\ HCl \longrightarrow 2\ NaCl + H_2S_2O_3,$$
$$H_2S_2O_3 \longrightarrow H_2O + SO_2 + S.$$

The sodium salt is the photographer's "hypo." The name indicates that the acid differs from sulfuric acid in containing one sulfur atom in place of the fourth oxygen. "Hypo" reacts with free chlorine, and so is a good "antichlor" after bleaching.

Pyrosulfuric Acid, a good oxidizing agent, is formed when sulfuric acid and sulfur trioxide are brought together in molecular proportions. Its salts are easily prepared by heating acid sulfates:

$$2\ KHSO_4 \longrightarrow H_2O + K_2S_2O_7.$$

Persulfuric Acid ($H_2S_2O_8$) is a rather modern oxidizing agent of great power. Electrolysis of a cold concentrated solution of an acid sulfate with a wire as anode produces the salts of persulfuric acid. The acid sulfate ionizes as follows:

$$KHSO_4 \rightleftarrows \overset{+}{K} + H\overset{-}{S}O_4.$$

The HSO_4^- ions on discharge at the small anode (high current density) unite with each other to form $H_2S_2O_8$. The acid potassium sulfate present promptly reacts with this unstable acid to form the sparingly soluble potassium persulfate, $K_2S_2O_8$. Ammonium persulfate is finding some use in photography and as a general oxidizing agent.

Sodium Hyposulfite, $Na_2S_2O_4$, is made by the action of zinc and an excess sulfurous acid on sodium bisulfite:

$$Zn + 2\ NaHSO_3 + H_2SO_3 \longrightarrow 2\ H_2O + ZnSO_3 + Na_2S_2O_4.$$

Its solution has great reducing power and is used to reduce blue indigo (insoluble) to indigo white (soluble) so that the dye can penetrate fabrics in the vat. Later oxidation converts the colorless product back to the blue, insoluble indigo.

Polythionic Acids are made by passing hydrogen sulfide and sulfur dioxide alternately into water (very slow reaction).

$$H_2S + 3\ SO_2 \longrightarrow H_2S_4O_6,$$
$$2\ H_2S + 6\ SO_2 \longrightarrow H_2S_3O_6 + H_2S_5O_6.$$

Polythionic acids are always formed when sulfurous acid reacts with finely divided sulfur. When thiosulfates are acidified (releasing finely divided sulfur and sulfur dioxide in water) in the presence of an arsenite a large yield of pentathionic acid, $H_2S_5O_6$, is obtained. In the absence of the arsenite only traces of thioacids are formed.

EXERCISES

9. What volumes of H_2S and SO_2 (standard conditions) will react to give 30 g. of sulfur?

10. By analysis a compound is found to consist of 23.7 per cent sulfur, 23.7 per cent oxygen, and 52.6 per cent chlorine. Its molecular weight is 135.2. What is its formula?

11. What weight of sulfur dioxide can be prepared from 35 g. of sodium sulphite (95 per cent pure) and sulfuric acid?

12. What weight of pure sulfuric acid can be made from 1000 tons of pure sulfur? From 1000 tons of pure FeS_2?

13. Give four methods of making calcium sulfate.

14. Draw a "Sulfur Tree" somewhat like the "Oxygen Tree" on page 37.

15. How could you distinguish between a sulfide, a sulfite, and a sulfate (if all were soluble)?

16. What is the greatest difficulty in working the contact process for the manufacture of sulfuric acid?

17. Start with hydrogen, oxygen, sodium, calcium, carbon, chlorine, sulfur, platinum and feel free to use heat or light. What compounds can you make, using these elements? How would you do it? Omit platinum compounds.

18. At one time in England starch was treated with very dilute sulfuric acid (instead of pure hydrochloric acid) in order to convert the starch into glucose for the brewer. Many cases of arsenic poisoning developed among beer drinkers. What was the source of the arsenic?

CHAPTER XX

THE PERIODIC SYSTEM. ATOMIC NUMBERS

Similarity of Sulfur, Selenium, and Tellurium.—These three elements resemble each other in many respects, and between sulfur and selenium the likeness is remarkable. In fact, selenium usually occurs associated with sulfur in metallic sulfides. All three form similar compounds with hydrogen and oxygen and their acids and salts are much alike. Valence is the same for the three elements.

Compounds of Sulfur, Selenium, and Tellurium

H_2S	Hydrogen sulfide	H_2Se	Hydrogen selenide	H_2Te	Hydrogen telluride
SO_2	Sulfur dioxide	SeO_2	Selenium dioxide	TeO_2	Tellurium dioxide
H_2SO_3	Sulfurous acid	H_2SeO_3	Selenious acid	H_2TeO_3	Tellurous acid
Na_2SO_3	Sodium sulfite	Na_2SeO_3	Sodium selenite	Na_2TeO_3	Sodium tellurite
H_2SO_4	Sulfuric acid	H_2SeO_4	Selenic acid	H_2TeO_4	Telluric acid
Na_2SO_4	Sodium sulfate	Na_2SeO_4	Sodium selenate	Na_2TeO_4	Sodium tellurate

The comparison in the above table is worth noting. All three elements burn with pale blue flames to form the dioxides. Although sulfur dioxide is a gas, the other two are white solids, observed as a smoke when the elements burn. The oxides of sulfur and selenium react with water, but so far it has not been possible to hydrate the oxide of tellurium directly:

$$SO_2 + H_2O \rightleftarrows H_2SO_3,$$
$$SeO_2 + H_2O \rightleftarrows H_2SeO_3,$$
$$H_2TeO_3 \longrightarrow TeO_2 + H_2O \text{ (not reversible).}$$

Both selenious and tellurous acids are easily reduced to the element:

$$H_2SeO_3 + 2\ SO_2 + H_2O \longrightarrow Se + 2\ H_2SO_4.$$

Strong oxidizing agents convert the elements into sulfuric. selenic, or telluric acids.

$$S \longrightarrow H_2SO_4,\ Se \longrightarrow H_2SeO_4,\ Te \longrightarrow H_2TeO_4.$$

Each of the three elements reacts directly with metals when heated.

$$\begin{gathered} Fe + S \longrightarrow FeS, \\ Fe + Se \longrightarrow FeSe, \\ Fe + Te \longrightarrow FeTe. \end{gathered}$$

When these compounds are acidified poisonous gases of offensive odor are released.

$$\begin{gathered} FeS + 2\ HCl \longrightarrow FeCl_2 + H_2S, \\ FeSe + 2\ HCl \longrightarrow FeCl_2 + H_2Se, \\ FeTe + 2\ HCl \longrightarrow FeCl_2 + H_2Te. \end{gathered}$$

Although hydrogen sulfide has an offensive odor, hydrogen selenide is worse; it smells like rotten horseradish.

Selenium.—Selenium is non-metallic and exists in allotropic forms. The red form is obtained by reduction of selenious acid solutions and the black form by melting the red.

Berzelius discovered this element (1817) in the flue dust of pyrite burners. Selenium colors glass a rose-red and so can neutralize the green tint of ferrous iron impurities. During the World War the importation of Brazilian manganese into the United States was cut off through lack of ships. Selenium replaced manganese dioxide as a glass decolorizer, and has now been adopted as the standard by the glass industry of the world. Manganese dioxide is cheaper but not so reliable in use. The annual yield from the copper slimes (from electrolytic refining) is now about 125,000 lbs. of selenium. Red signal glass is made with selenium.

A small demand has been created by one of the curious properties of the element. Selenium conducts electricity better when exposed to light. Consequently it can be used in automatic devices for lighting buoys at night and cutting off gas flow at daylight. The selenium cell for measuring the light from stars depends on this property.

There is a possible use of organic selenium compounds in the manufacture of rubber for specialized uses. This was suggested by the similarity of selenium to sulfur.

Selenium in sufficient quantity imparts a ruby color to zinc-potash glass in the presence of cadmium sulfate and a reducing agent. Probably colored polyselenides are formed.

Selenium compounds have some value (and some hazards) as fungicides.

Tellurium.—Tellurium is rather plentiful as gold telluride in Colorado and other mining districts, but the small quantities made so far have been extracted from the anode mud of electrolytic copper refining. There are at present facilities for making 125,000 pounds per year in this country. Tellurium has been known since 1783, but at present there is no considerable use for it. Research is needed to make it useful. To-morrow it may become invaluable to us. Half a ton represents the present annual demand.

Tellurium dioxide is more acidic than basic, consequently salts formed by the union of TeO_2 with acids, even strong acids, are hydrolyzed on dilution, all the more because of the insolubility of tellurous acid, and its weak ionization.

Some tellurium compounds have a toxicity against certain bacteria comparable to that of phenol (carbolic acid).

The Periodic System

Ever since the establishment of the atomic theory by Dalton and Berzelius, chemists have looked for some relation between the atomic weights of the elements and their properties. The development of this relation was delayed a half century because the conception of the atom became increasingly vague in spite of the brilliant work of Dalton, Berzelius, and Avogadro.

In order to come to some general understanding on atomic weights an international convention was held in 1860, and at this Cannizzaro showed the necessity of reasoning from Avogadro's hypothesis in the development of any system of atomic weights. This clarified the situation so that the epochal work of Mendeleeff and Meyer in 1869 became possible. As Wadmore says, "prior to this epoch, errors and inconsistencies must necessarily have masked any general relation between the properties and atomic weights of the elements, though vestiges of such a regularity had been observed."

It had been known that some elements were metallic or base forming and the others non-metallic or acid forming. An attempt could have been made to use valence as a means of classifying elements, but this has many faults, for sodium and chlorine do not resemble each other at all, although of the same valence, and besides, several elements have more than one valence. The first ray of light on this subject appeared in 1829, when Döbereiner observed that several groups of three elements each could be so arranged that the atomic weight of one was the average of the other two and in all such cases the three elements strikingly resembled each other in properties. Chlorine (35.5), bromine (79.9), and iodine (126.9) show these relations, as the student well knows by this time. The relations are just as convincing for sulfur (32), selenium (79.2), and tellurium (127.5). Calcium (40.1), strontium (87.6), and barium (137.4) are yet to be studied, but resemble each other very closely indeed. The acceptance of Cannizzaro's ideas on atomic weights put new life into ***Döbereiner's triads.*** Then in 1863 Newlands, the English chemist, announced a farther-reaching relation. He arranged the elements, beginning with lithium (not hydrogen), in order of increasing atomic weight and found that "the eighth element, starting from a given one, is a kind of repetition of the first, like the eighth note of an octave in music":

Li	Be	B	C	N	O	F
6.94	9.1	11	12	14.01	16	19
Na						
23, etc.						

Newlands read his paper before the Chemical Society of London and it was ridiculed by many chemists. Twenty-one years later he was honored with the Davy medal for his vision.

Although apparently unaware of Newlands' ideas, it was only a few years (1869) until the great Russian, Mendeleeff, outlined the periodic relations much as we know them to-day. Quite independently the German, Lothar Meyer, made a similar discovery, and the credit should be divided. Mendeleeff developed the "periodic law" more fully and brilliantly than Meyer. His table, modified and brought up to date, is given below. As he stated the law, "The whole of the properties of the elements, both chemical and physical, vary in a periodic fashion with their atomic weights."

The column headed "Group O" was unknown to the authors of the system. Proceeding from lithium to the right, the chemical and physical properties steadily change. If we went no farther than fluorine, we might insist that any property of the elements changes steadily with increase in atomic weights. But such a theory would be rejected upon proceeding to the heavier element, sodium. The base-forming property steadily decreases from lithium to fluorine, but with sodium it returns in full strength. Beginning with sodium the base-forming property, for example, again decreases until potassium is reached. But potassium hydroxide is a still stronger base than sodium hydroxide. In other words ***the properties of the elements are periodic functions of their atomic weights.***

The table is so arranged that the ninth, seventeenth, etc., elements begin new horizontal rows or periods. It is seen at once that elements in the same vertical column resemble each other in valence, base-forming properties, etc. Lithium, sodium, potassium, rubidium, and cæsium are all monovalent, their hydroxides are strong, and nearly all their compounds are soluble. Moreover the free metals all react violently with water, displacing hydrogen. It can be no accident that an arrangement in periods of nine brings these elements in the same vertical column or "Group," as we call it. Nor is it an accident that sulfur, selenium, and tellurium occur in the same column. Our study of the halogens prepares us to be properly impressed by the placing of chlorine, bromine, iodine, and fluorine in the same group. In fact it is difficult to find any two elements of marked similarity in different columns.

THE RARE EARTH METALS ARE

57 La 139	58 Ce 140.2	59 Pr 140.6	60 Nd 144.3	61 Il ?	62 Sa 150.4
63 Eu 152	64 Gd 157.3	65 Tb 159.2	66 Dy 162.5	67 Ho 163.5	68 Er 167.4
69 Tm 168.5	70 Yb 172	71 Lu 174			

Periodic Table showing Atomic Numbers in Red

Period	Group 0	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
0		1 H 1.008							
I	2 He 4.002	3 Li 6.940	4 Be 9.02	5 B 10.82	6 C 12.000	7 N 14.008	8 O 16.000	9 F 19.00	
II	10 Ne 20.183	11 Na 22.997	12 Mg 24.32	13 Al 26.97	14 Si 28.06	15 P 31.02	16 S 32.06	17 Cl 35.457	
III	18 A 39.94	19 K 39.10	20 Ca 40.07	21 *Sc* 45.10	22 *Ti* 47.9	23 *V* 50.96	24 *Cr* 52.01	25 *Mn* 54.93	26 *Fe* 55.84 27 *Co* 58.94 28 *Ni* 58.69
		29 *Cu* 63.57	30 *Zn* 65.38	31 *Ga* 69.72	32 *Ge* 72.60	33 As 74.96	34 Se 79.2	35 Br 79.916	
IV	36 Kr 82.9	37 Rb 85.44	38 Sr 87.63	39 *Y* 88.92	40 *Zr* 91.22	41 *Cb* 93.1	42 *Mo* 96.0	43 *Ma* ?	44 *Ru* 101.7 45 *Rh* 102.91 46 *Pd* 106.7
		47 *Ag* 107 880	48 *Cd* 112.41	49 *In* 114.8	50 *Sn* 118.70	51 Sb 121.77	52 Te 127.5	53 I 126.932	
V	54 Xe 130.2	55 Cs 132.81	56 Ba 137.36	57-71 Rare-Earths	72 *Hf* 178.6	73 *Ta* 181.5	74 *W* 184.0	75 *Re* 188.7	76 *Os* 190.8 77 *Ir* 193.1 78 *Pt* 195.23
		79 *Au* 197.2	80 *Hg* 200.61	81 *Tl* 204.39	82 *Pb* 207.22	83 Bi 209.00	84 Po 210.0	85	
VI	86 Rn 222.0	87	88 Ra 225.97	89 Ac ?	90 Th 232.12	91 U-X ?	92 U 238.14		

The *atomic number* appears before the symbol of each element in red and the *atomic weight* below. The atomic weights of Po, Ac, and U-X are uncertain values. With atomic numbers 81–84 and 88–92 are to be assigned a number of other elements, for the most part radioactive, which have the same chemical properties as the element in the table but somewhat different atomic weights.

The third series beginning with potassium includes two octaves, potassium to manganese and copper to bromine, and is called a long series. Iron, cobalt, and nickel are transition elements bridging the gap between the two simple octaves. The fourth and fifth are also long series with transition groups.

The fifteen rare earth metals, with a usual valence of three, occur together in monazite sand and are hard to separate.

Valence Changes.—The elements of Group O are so inactive that they have no combining power at all, therefore no valence. In Group I all elements are monovalent and their oxides are such as Na_2O or Ag_2O (general formula, R_2O). In Group II the valence increases to two. Their oxides are such as CaO or ZnO (general formula RO). Towards oxygen the maximum valence of the different groups rises regularly to seven (R_2O_7) but toward hydrogen (or chlorine) the valence rises only to four (in Group IV) and then steadily falls to one. Chlorine in Group VII is found in Cl_2O_7 and in HCl.

Property Changes.—The elements of Group I form strong bases, those of Group II only moderately strong bases, and in the middle groups, III and IV, the hydroxides are weakly basic or even weakly acidic, as in carbonic acid. Remember that most acids as well as all bases are hydroxides. Aluminum hydroxide ionizes both as a weak acid and a weak base, an "amphoteric" electrolyte, as is zinc hydroxide. In Group V the elements form strong acids, such as phosphoric and nitric. Group VI permits the formation of strong acids, such as sulfuric and chromic, and of course Group VII is the source of the halogen acids. At the left the columns are strongly basic, at the right strongly acidic, and in the middle the elements resemble both types.

Meyer was especially interested in the regular, periodic variation in such properties as melting point, density, and malleability. These change in much the same way as basicity and acidity.

There is a steady change of properties vertically as well as horizontally in the table. In any given vertical column density increases from the top to the bottom, as does the metallic character. In Group V the stability of hydrides decreases towards the bottom. Compare NH_3, PH_3, AsH_3, and SbH_3.

The Rare Gases.—Mendeleeff knew nothing of Group O. When these six elements were discovered they fitted in very well as a transition group connecting the extremely acidic elements of

Group VII with the extremely basic elements of Group I. Since they are quite inactive, they have no valence and form no hydroxides.

Sub-groups.—Below sodium in Group I we observe that copper, silver, and gold resemble the rest of the family mainly in valence, but resemble each other in several other ways. In Group II the zinc, cadmium, and mercury make a good family, but are not remarkably like barium, calcium, and strontium. In Group VII manganese has but little relation to the halogens. So each column is divided into two sub-groups, A and B, written at the two sides of the column.

The queer position of iron, nickel, and cobalt (queer in consideration of their valence) is explained by J. J. Thomson as an example of an increase in the positive charges of the atomic nucleus by one without the occurrence of an additional valence electron in the outer shell of the neutral atom. This additional compensating electron went into an inner shell. Thus atomic weight increased while valence did not.

Defects of the Periodic System.—It is difficult to place hydrogen in this system, but it is usually written in Group I because of its valence and the fact that it becomes a positive ion.

Tellurium is next heavier than iodine, and yet if placed in this order iodine would not be grouped with chlorine, bromine, and fluorine where it belongs, nor would tellurium be listed in the company of sulfur and selenium. The temptation to change places, thus putting these two elements where their properties clearly indicate they belong, is irresistible. But, written as they are in all tables, the consecutive order is broken down. Of course many attempts were made to prove that the atomic weights recorded are in error or to show that tellurium is really a compound. All of these failed. Equally annoying is the argon-potassium situation. A glance at the table shows that each conforms to the rule about "birds of a feather." But another glance at their atomic weights indicates that their places in any regular order have been interchanged.

Exercise 1.—An element is discovered with compounds similar to those of manganese. From the analysis of its chloride the equivalent weight is found to be 49.4. What is the atomic weight? Why?

Another weak point is the lack of quantitative relations. It is all qualitative—the properties change in a general way. And it seems unfortunate that manganese must be grouped with the halogens which it resembles so slightly. There are other examples of ill-matched elements. Furthermore only one valence is considered. The rare earths with a general valence of three do not fit in.

Advantages of the Periodic System.—Although we admit the imperfections of the system, we are convinced of the existence of a fundamental relation between properties and atomic weights. It has been of the greatest service in more ways than one. We place the following to its credit:

1. Classifying Facts. As an aid in classifying a multitude of separate facts it helps the memory and makes for clearness.

2. Predicting New Elements. By its help new elements have been predicted. A few of them were discovered later. In order to place elements where their properties indicate they belong gaps must be left here and there in the periodic table. The assumption is that elements exist (if we could only find them) which occupy the gaps. And from their position remarkable predictions as to their properties have been made. Mendeleeff was bold enough to predict the existence of the elements we now know as scandium, gallium, and germanium. In a few years all three were discovered as a result of this prediction.

Mendeleeff made no predictions about Group O, but after the discovery of argon and helium it was evident to Sir William Ramsay, the English chemist, that there were places for three more inert gases. As the result of brilliant investigation he discovered three such gases and named them neon, krypton, and xenon. Predictions were completely fulfilled in this instance. There is, however, something yet to be done in filling in the gaps. Mendeleeff predicted an element between molybdenum and ruthenium. He placed it in Group VII and called it ekamanganese. For this we are still waiting.

It is now believed that this missing element is a halogen of atomic weight 218, a jet-black solid with metallic luster, a density of about 8, and a melting point about 230°. It is probably nearly insoluble in water, not very active and should be displaced from its simple compounds by free iodine. Doubtless it will be discovered associated with iodine.

Hafnium, number 72, was discovered about 1923 by Coster and Hevesy (Copenhagen) by X-ray examination of zirconium-bearing minerals. It is very difficult to separate chemically from zirconium salts.

The discovery of Rhenium (number 75) and Masurium (number 43) in 1925 by Noddack, Tacke and Berg (Berlin) from X-ray spectra of platinum ores is still in question. If admitted as accurate only two of the possible 92 elements are left to discover, number 85 a halogen, and 87 an alkali metal.

3. Correcting Atomic Weights. The failure of certain elements to fall into the group to which they evidently belong has always led to very careful redetermination of their atomic weights and in some instances errors have been discovered. This was notably true of cæsium, which had been given an atomic weight of 123.4. The logic of the table indicated that this was surely too low. More accurate work gave us 132.8 as the correct value quite in keeping with the Periodic Law. Mendeleeff insisted that the known atomic weights of uranium and beryllium (glucinum) must be wrong. Later a study of vapor densities of their volatile compounds revealed the predicted errors.

The periodic system has aided in the determination of atomic weights of elements whose compounds are not gaseous. For example, the combining weight of radium indicated possible atomic weights of 113 with RaCl as a correct formula or 226 with $RaCl_2$ as a correct formula. But radium resembles the divalent calcium and barium rather than monovalent sodium and potassium. Consequently $RaCl_2$ and an atomic weight of 226 were agreed upon. Of course the law of Dulong and Petit could have been used in deciding between the possible atomic weights of radium.

4. Stimulating Research. As already shown, the gaps in the table inspire diligent effort to fill them. To this inspiration we owe the discovery of several new elements. And, as explained in detail, apparent errors in the table have led to corrections of several atomic weights. The relation of properties to atomic weights has been of the greatest value in all sorts of inorganic research and has even led to important corrections of supposed properties.

Other Classifications of Elements.—It is admitted that the periodic grouping of the element in accordance with the atomic weights is not perfect. These imperfections are removed when the periodic grouping is based on ***atomic numbers*** instead of atomic weights.

ATOMIC NUMBERS

It has been known for more than a quarter of a century that the cathode rays (a stream of electrons) on striking any substance in their path produce the vibrations known as X-rays. It was not until 1914 that Moseley, a young English physicist, measured the wave lengths of these rays emanating from different metals used as anti-cathodes in an evacuated X-ray tube. He made each of the metals the target (anti-cathode) of an X-ray bulb. The X-rays were then passed through a thin crystal of potassium ferrocyanide on to the photographic plate. From the photographic spectra secured he calculated the wave lengths. These wave lengths decrease in a regular way with increasing atomic weight. In fact Moseley found a simple numerical relation between the wave lengths of the most intense lines in the different X-ray spectra. He expressed this relation in a series of values called ***atomic numbers.*** Strangely enough, these are all whole numbers. The atomic numbers are approximately half the atomic weights, and represent, in reality, the number of free positive charges of electricity (protons) in the nucleus of the atom of each element. In addition to the free protons there are (except in the case of hydrogen) some additional protons bound by an equal number of electrons. Other electrons are placed in the outer shells of the atom. This excess of protons in the nucleus is electrically balanced in the neutral atom by an equal number of planetary electrons, hence the atomic number is measured either by the number of free protons in the nucleus or by the number of planetary electrons.

The atomic numbers 59–72 belong to the metals of the "rare earths," not listed in the table. Hafnium with an atomic number of 72 has been discovered since Moseley prepared the table above.

It is evident that this is superior to the periodic system of Mendeleeff, for the consecutive order is here used for argon and potassium as well as for iodine and tellurium without spoiling the group arrangement by properties. The fundamental character of an element is determined by its nuclear charge more than by its atomic weight.

In the light of these findings the Periodic Law may be reworded with exactness. The chemical properties of the elements are a periodic function of their position in a series determined by their

X-ray spectra. Or, more briefly, ***the chemical properties of the elements are a periodic function of their atomic numbers.***

Moseley's atomic number rule furnished definite information as to the existence and location of gaps in the Periodic Table; it gave a basis for calculation and identification of the X-ray spectrum of a looked-for element; and finally offered a method of recognizing in a mixture two elements so similar in chemical properties as to be almost inseparable.

The American chemist, B. S. Hopkins, believing that the missing element of atomic number 61 shared the striking similarity in properties and occurrence of the "rare earth" elements, looked for it in the residues from monazite sands, a mineral rich in elements 60 and 62. By means of laborious salt formation from 400 pounds of residues, by fractional crystallization, and concentration, a material was at last obtained that showed spectroscopic bands calculated for the missing element. After confirmation by X-ray analysis the element was named Illinium in honor of the University of Illinois where Hopkins is a professor of chemistry.

REFERENCES

"Illinium" (B. S. Hopkins), *Science, 63*, 575, (1926).

CHAPTER XXI

STRUCTURE OF THE ATOM. RADIOACTIVITY

Radioactivity

X-rays.—Röntgen, in 1895, observed mysterious radiations, "X-rays," proceeding from Crookes electric discharge tubes (high vacua) and penetrating supposedly opaque substances such as paper, wood, flesh, and fabrics. These rays were secondary, that is, they were started by the impact of cathode rays on glass or other substance in their path. The fact that bones, metals, and certain other substances were opaque to the X-rays made possible photographs of great use. For example, a needle or bullet could be located in the flesh. It is possible with the modern very penetrating X-rays to locate flaws only 1.5 mm. thick in 7.5 cm. steel plates. Fig. 77 represents a modern X-ray bulb.

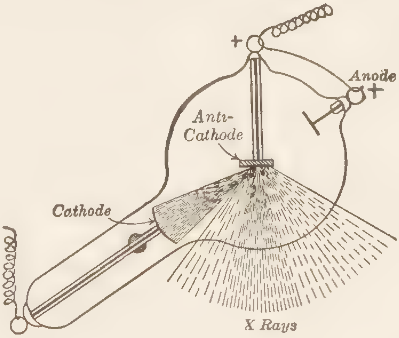


FIG. 77.

Becquerel Rays.—Henri Becquerel in 1896 conceived the idea that perhaps any fluorescent or phosphorescent substance might be a source of similar penetrating rays. He wrapped photographic plates in black paper and laid on them many such substances. Only one, potassium uranyl sulfate, $K_2UO_2(SO_4)_2$, produced any effect on the photographic plate. From this beginning Becquerel proceeded to show that any uranium compound gave off these penetrating "Becquerel rays" and that they discharged the metallic leaves of an electroscope (Fig. 78). Later, Rutherford showed that this was due to ionization of air molecules surrounding the leaves. With the electroscope one billionth of a gram of radium can be detected.

Radium.—Because of Becquerel's work with the penetrating radiations from uranium compounds the Curies (Madame Marie and her husband, Professor Pierre Curie of the Sorbonne) decided to examine some of the residues from pitchblende, a uranium mineral, after all the uranium had been extracted. They found that these residues gave off similar but more powerful radiations than the uranium salt itself.

"Their next task was to separate the elements or compounds that had this property. By the ordinary methods of chemical analysis they separated the various elements found in pitchblende residues and tested each for radioactivity, or Becquerel radiations, as it was then called. Most of the elements separated showed no activity.

"However, when bismuth was reached in the analysis it was found that it was intensely active. But since ordinary bismuth or bismuth compounds produced no radiations of this kind it was assumed that a new element closely associated with it in chemical properties had been separated with it. The active substance of the bismuth precipitate was separated, and this was named ***polonium*** by Madame Curie after her mother country, Poland. This was the first of the radium series to be discovered. Again as the barium was separated, this was found to be intensely active, and as ordinary barium compounds or minerals do not possess this property it was concluded that another element similar to barium had been separated with it at this stage. And by separating this active material from the barium a new element was discovered, possessing an activity at least 1,000,000 times that of uranium. This was the new element—***radium***."

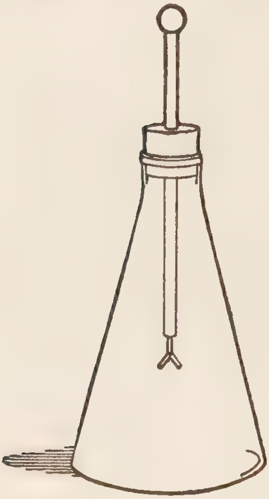


FIG. 78.—An electroscope.

In 1910 Madame Curie completed her brilliant work by isolating the element radium. She electrolyzed an aqueous solution of radium bromide, using a mercury cathode. The radium deposited in the mercury was secured by distilling off the latter metal. The radium prepared looked like metallic calcium or barium and acted like them. It quickly tarnished in the air and decomposed water at a moderate speed. Its carbonate and sulfate were insoluble and its hydroxide a moderately strong base. In short, radium so completely resembled barium, calcium, and strontium in properties that it had to be placed in Group II of the periodic table. Its valence is 2.

To find the exact atomic weight of radium was a simple matter when the element was known to be divalent. Analysis of the chloride showed the proportion by weight of chlorine and radium to be 35.46 : 113; therefore, the formula must be $RaCl_2$ and the atomic weight of radium 226.

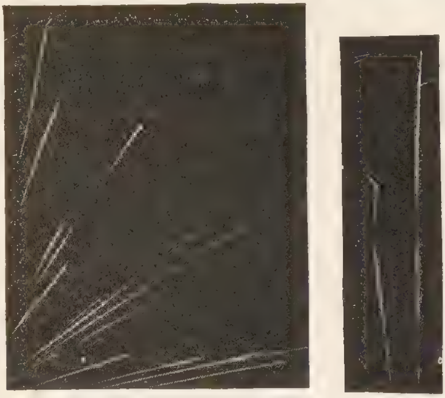


FIG. 79.—Fog tracks of radium rays.

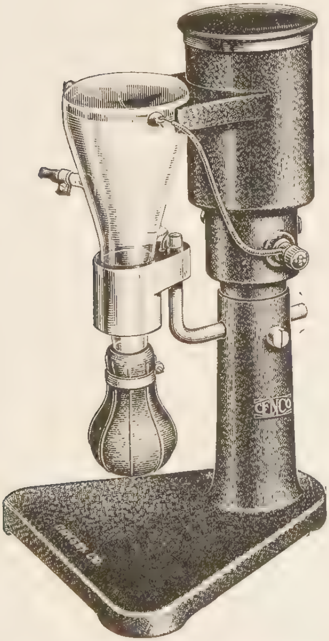


FIG. 80.—Fog track apparatus.

Radium Rays.—Soon after the discovery of radium it was developed that it gives off three types of radiations. The ***alpha rays*** are positively charged atoms of ***helium*** moving 20,000 miles per second. They do not actually travel 20,000 miles, however, in any time; they are stopped completely before they have gone 8 cm. through the surrounding air. After colliding with several thousand air molecules their initial velocity is reduced to nothing. But they produce very appreciable effects while traveling. Much heat is developed and as they smash through about 200,000 air molecules some of the latter have electrons knocked out of them and thus become ionized particles.

Now ionized gas molecules act as nuclei for the condensation of moisture just as well as do dust particles. C. T. R. Wilson showed this very cleverly by placing a bit of radium in a bulb of air saturated with water vapor. On sudden cooling, the drops of moisture condensed as fog wherever ionized air molecules existed. Wilson photographed these fog tracks, thus showing the path of an alpha particle. This experiment furnished convincing evidence of the existence of atoms and molecules.

The collision between an alpha particle and a crystal of zinc sulfide is marked by a visible flash of light. The ***spinthariscope*** (Fig. 81) is a simple contrivance for magnifying this effect. At one end of a small tube is a zinc sulfide screen and near this is a minute speck of a radium salt. At the other end of the tube is a lens to magnify the flash of light when an alpha particle hits the screen. The human eye needs fifteen or twenty minutes of rest in darkness before it is possible to observe the faint flashes of light. It is decidedly impressive to see the work of a single atom and to realize that this bombardment continues for thousands of years. These alpha rays are able to decompose water, to convert oxygen into ozone, and to bring about the union of hydrogen and chlorine.

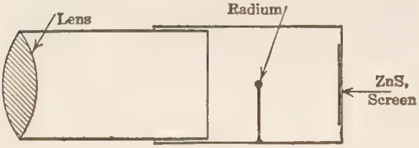


FIG. 81.—Spinthariscope.

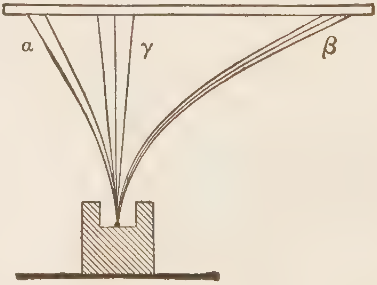


FIG. 82.—Effect of a magnetic field on radium radiations.

The ***beta rays*** are identical with cathode rays, but move faster and are 100 times as penetrating. These cathode radiations and beta rays are known to be merely streams of electrons. When thrown off by radium they move 180,000 miles per second (the velocity of light). Since they have only 1/7400 the mass of alpha particles, they are deflected much more by a magnetic field (Fig. 82). As negative particles they are deflected in the opposite direction from alpha particles. In spite of their tremendous initial velocity, they are completely absorbed after smashing through 1 cm. of water or 1 mm. of lead or 4 mm. of aluminum and causing some ionization of atoms.

The ***gamma rays*** resemble X-rays but are far more penetrating. They are electromagnetic disturbances, not streams of small particles, and hence are not deflected in a magnetic field. Alpha particles are stopped by 0.1 mm. thickness of aluminum foil, beta rays by 4 mm. thickness, and gamma rays by 1 ft. of iron.

The Disintegration of Radium.—Rutherford (then at McGill University) was the first to suggest (1902) that radium actually breaks down by throwing off other elements at great velocity. Ramsay and Soddy proved that the alpha particles are atoms of helium. Rutherford later secured a gas from radium which he condensed by cooling in liquid air and volatilized on warming. This peculiar gas was itself radioactive, although this activity disappeared in less than a week. It was called "radium emanation" until Ramsay, working with a few cubic millimeters, determined its molecular weight (222.4) and named it ***niton,*** now *radon.*

A series of disintegration products has been discovered starting with uranium and, by twelve intermediate products, ending with lead. Since all uranium compounds or minerals are radioactive, they must contain radium. One gram of radium in one year gives off 167 cu. mm. of *helium* gas. By counting the number of alpha particles emitted per second from a minute portion of radium (containing a known number of radium atoms) it has been estimated that half of the radium atoms will have decayed in about 1690 years.

RaC is now thought to lose one electron in passing into RaC_1 which exists for only one millionth of a second before changing into RaD, with loss of a helium atom.

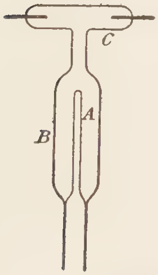


Fig. 83.—The formation of helium.

The first definitely established example of transmutation of one element into another was observed and tested by Rutherford in 1909. Using the glass apparatus represented by Figure 83, he evacuated the tubes *B* and *C* and filled *A* with helium under slight pressure. No spectroscopic trace of helium could be observed in *C* during an electric discharge between the two wires. This proved that helium could not leak through the tube *A*. This inner tube *A* was made from glass less than 0.01 millimeter in thickness, so that alpha particles could penetrate it, if given opportunity. Having tested for leaks, Rutherford now filled *A* with radon, the gaseous emanation from radium. In a few hours the spectrum of helium was observed in *C*.

If all the radium associated with a uranium salt is removed, the remaining salt gradually recovers its activity; that is, more radium is formed from the uranium. Thus there is a definite ratio of radium to uranium in any uranium ore (1 : 3,000,000), resulting from a balance between the rate of formation and rate of decay of radium. All the radium in the world to-day is younger than the human race.

This conception of radium seems to shake our definition of an element, but it need not. We are unable to start, stop, hasten, or retard this disintegration. In liquid air or the electric furnace, radium calmly goes on the even tenor of its way, supremely indifferent to the frantic efforts of mere human beings. So we rest on the conception of an element as a substance not readily decomposed in ordinary chemical processes. No perfectly satisfactory definition has yet been given. In the radium disintegration series on this page "He" represents an escaping helium atom and "E" an electron. The half-life and atomic weight of each element is given. Small decimal fractions are omitted.

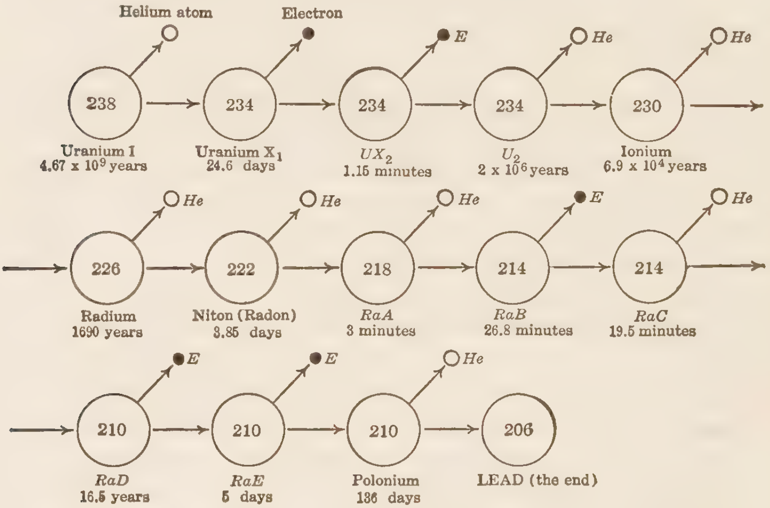

Helium atom
Electron
E
He
He
238
234
234
234
230
Uranium I 4.67 x 10⁹ years
Uranium X₁ 24.6 days
UX₂ 1.15 minutes
U₂ 2 x 10⁶ years
Ionium 6.9 x 10⁴ years
He
He
He
E
He
226
222
218
214
214
Radium 1690 years
Niton (Radon) 3.85 days
RaA 3 minutes
RaB 26.8 minutes
RaC 19.5 minutes
E
E
He
210
210
210
206
RaD 16.5 years
RaE 5 days
Polonium 136 days
LEAD (the end)

FIG. 84.—Disintegration of elements in the radium series. Half-life.

It is a startling fact that lead occurring in uranium ores has an atomic weight of 206, while common lead has an atomic weight of 207.2. To add to the novelty the atomic weight of lead associated with thorium (also radioactive) is 208.4. Remember that the weight of an electron is negligible, only 1/1845 that of a hydrogen atom, and that a helium atom has a weight of 4. Now check the weights in the uranium-radium-lead series above and it will be apparent that the final product, lead, must have an atomic weight of 206 rather than 207. Extremely accurate atomic weight determinations by Richards of Harvard gave the same result. These three forms of lead, with identical chemical properties and different atomic weights, are called ***isotopes.***

Energy of Radium.—One gram of radium gives off more than enough heat to melt its own weight of ice every hour, to be exact, 132 cal. This heat is the result of the collisions of alpha and beta particles with surrounding substances. When atoms unite with each other as in ordinary reactions, it is evident that only a minute fraction of the total energy locked up in the atoms is released. We may or may not find the key to this vast storehouse of energy. It has been calculated that *if* one pound of hydrogen shifted its atomic structure into that of helium the energy released would equal that of 10,000 tons of coal.

Uses of Radium.—The chief use of radium today is as a therapeutic agent. Its radiations have a greater effect on unhealthy tissue than on normal tissue, and so, if properly managed, it is possible to destroy cancerous tissue *on the surface* of the body and to relieve pain. Penetrating X-rays can also be used for cancer treatment except where mechanical difficulties intervene. Radium emanation is much used in hospitals because it can be applied conveniently in small tubes or needles and its use permits the radium itself to be locked up in a safe or applied to a particular case. More emanation is constantly being formed.

Too long an exposure to any considerable quantity of radium causes dangerous burns, so the powerful material is kept in thick lead tubes. Glass tubes containing it develop a violet or brown color. Some gems are affected.

Most radium is converted into the insoluble sulfate to prevent loss from possible water contact in handling.

A luminous paint is prepared for *radiolite* watch faces, door numbers, etc., by mixing 100,000 parts of phosphorescent zinc sulfide with from 1 to 10 parts of a radium salt. The action is the same as in the spinthariscope. About 15 cents' worth is used on a single watch.

Far more important than its use in therapeutics is the light that radioactivity has thrown upon the problems of the constitution of matter.

The Radium Industry.—Up to 1929 the world had produced 300 g. of radium (about 10 oz.) and this was not enough for the use of medical investigators. The price has fallen to $50,000 per gram, but even that does not discourage all purchasers. The pitchblende deposits of Bohemia are nearly exhausted and the only important source of the metal until recent years has been the carnotite ore of Utah and Colorado. This does not occur in a concentrated form and when worked up by four months of careful labor yields only 2 mg. of radium per ton. However in 1922 announcement was made of the discovery of a small but very rich deposit of pitchblende in the Katanga district (Belgian Congo). The price dropped immediately and American production ceased temporarily. One gram of radium is obtained from 9 tons of the Katanga ore, as compared with 1 g. from 400 tons of American ore. The value of all the radium obtained since 1898 is $20,000,000.

Other Radioactive Elements.—Thorium decays and yields a series of active products. With ten intermediate compounds it gives an end-product of lead The first product, mesothorium, is used as a cheaper substitute for radium. Unfortunately half the material decays in 6.7 years. The gamma rays from thorium D are the most penetrating known. Mesothorium decays at least 250 times faster than radium and hence in the pure state is more active than radium. *Actinium* and *polonium* are also radioactive.

It was recently found that a certain type of radio transmitter needed a high-powered, low-voltage vacuum tube. This need was met, when it was observed that a tungsten filament containing thoria operates with an astonishing increase in electron transmission, as compared with a pure tungsten filament. The thoria is reduced to thorium, which diffuses to the surface and there forms a continuous film one atom deep. The high affinity of thorium for tungsten prevents the surface thorium from evaporating, as it would if the whole filament were thorium.

Exercise 1.—What is the relation between X-rays and the different radiations from radium?

Exercise 2.—How is the worker protected from radium radiations?

Exercise 3.—How much radium has been obtained to date?

Exercise 4.—What are isotopes?

Structure of the Atom

The modern theories of atomic structure were developed after the facts of radioactivity became established—and in the light of these facts.

To Rutherford we owe the first suggestion of the accepted nuclear theory. According to this theory the neutral atom is a miniature solar system with a definite number of positive charges (protons) rather closely compacted in a central nucleus. Associated with the protons in the nucleus are a smaller number of negative charges (electrons). Surrounding the nucleus at relatively great distances are a number of electrons exactly equal in number to the excess of positive charges in the nucleus; hence the neutrality of such an atom.

As Aston puts it, "If in the atom of helium we take the nucleus as represented by a rather large pea, its planetary electrons may be represented as two rather smaller peas revolving around it at a distance of a quarter of a mile."

There are reasons for estimating the diameter of the nucleus as only about 1/10,000 that of the atom. If this is correct the nucleus has only one millionth the volume of the atom and a cubic centimeter of tightly packed nuclei would have a mass of about a million tons. This density is far beyond that of 50,000 attributed by some astronomers to the companion star of Sirius. However, there is no possibility of securing such close-packing.

Gilbert N. Lewis in 1916 advanced his startling ***"octet" theory,*** which in 1918 and later was so brilliantly applied and extended by Langmuir.[1] Some of the electrons in the atom are closely associated with the protons in the nucleus. According to Lewis, the remaining electrons are arranged around the nucleus in concentric shells.

In the rare gases (excepting helium) the outer shell contains eight electrons—and the atom is absolutely inactive chemically.

But with increasing atomic weight (due largely to increase in the protons of the nucleus) new outer shells are built up around the structure of the atom. Helium has a nucleus of four protons closely associated with two electrons and an outer shell of a *stable pair* of electrons. From this element we advance to lithium by surrounding the helium atom with an outer shell with places for eight outer electrons, but with only one such place occupied.

The next heavier element, beryllium, is built up by addition of a second electron to the same outer shell of lithium. Since we are speaking of the neutral atom another positive charge (a proton) must have been added to the nucleus at the same time, thus increasing the atomic weight. With the next elements in order of increasing atomic weight—boron, carbon, nitrogen, oxygen, fluorine, and neon—we find a steady increase of electrons in the outer shell until with neon (inactive) the shell is complete with eight electrons—an octet.

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[1] Langmuir holds that some outer shells are complete with 18 or 32 electrons so arranged as to give great stability. At this stage it is not essential that we consider anything more than the simplest form of the octet theory.

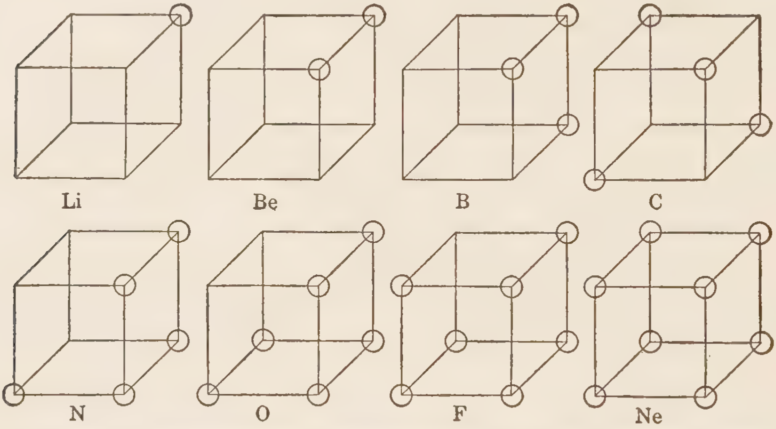


Fig. 85.—Valence electrons in the outer shells of lithium, beryllium, boron, carbon, nitrogen, oxygen, fluorine and neon.

Then another shell is added, incomplete, with one electron actually in place, but room for seven more, to form the atom of sodium. This shell may be gradually filled with electrons until with completion of its quota (eight) the atom of argon (inactive) is formed. Thus we see the periodic formation and filling in of outer shells, eight elements in each period building up from one to eight electrons for the outer octet.

As Lewis explained the formation of compounds the electron of an outer incomplete shell may be given to another atom, as in lithium, or enough electrons may be taken up by the incomplete shells of other atoms to complete the shell, as in fluorine, thus accounting for positive and negative valence. So with the formation of sodium chloride. The sodium atom gives its single outer-shell electron to the chlorine atom, which needs just one electron to complete its outer shell of eight. The two atoms are thus held together by electrical forces set up as a result of the electron shift.

Here is the proper explanation of valence. The lithium atom (like Na and K) has a positive valence of one because it tends to give away its single electron of the outer shell. Since the neutral lithium atom held positive charges (protons) equal in number to its negative charges (electrons) this loss of one electron leaves an excess of one positive charge. The lithium atom then has a positive valence of one in its compounds. Beryllium can give away its two electrons of the outer shell, thus showing a positive valence of two. Positive valence, evidently, is measured by the capacity of an atom to *give away* electrons. In ammonia nitrogen has *taken on* three electrons from three hydrogen atoms in order to complete its outer shell. The fluorine atom lacks but one electron to make an outer shell of eight so it can take up one from a willing hydrogen atom. Fluorine shows a negative valence of one in hydrogen fluoride, nitrogen in ammonia a negative valence of three. Of course, an element can give away all its outer-shell electrons and rely for stability on the complete octet beneath, or it can gain enough to fill out its incomplete layer. Thus nitrogen may show a negative valence of three in NH_3 and a positive valence of five in N_2O_5.

We may then call the electrons of an incomplete outer shell "valence electrons." Chemical reaction is merely a matter of transfer or sharing of these electrons. The preponderating tendency of every atom is toward an arrangement of electrons with eight in the outer shell, secured by either gain or loss of electrons.

This stable structure is secured in many instances when two atoms share between them a pair of electrons. This pair of shared electrons really represents the simple bond of valence.

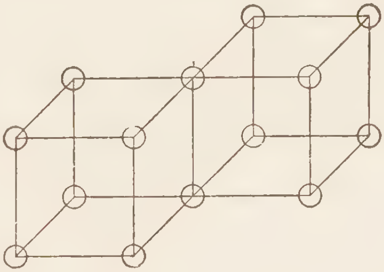


FIG. 86.—A non-polar molecule formed by the sharing process.

Compounds formed by the sharing of electrons do not ionize in solution (CCl_4 and CH_4, for example) and are called ***non-polar.*** Compounds such as NaCl contain atoms in which a transfer of electrons has already occurred, and the atoms are held together by electrical attraction. The positive and negative atoms are almost ionized and need only the separating help of some solvent such as water to become actual ions. Thus acids, bases, and salts are ***polar,*** like a magnet, and exert an attraction between whole molecules to build up aggregates, sometimes crystalline.

NOTE: Since the hydrogen atom contains one positive charge (proton) and only one electron, it may be stated that the proton is really the hydrogen nucleus with an atomic weight of 1.008. The electron has only 1/1845 of the mass of the proton, so its weight is negligible.

There are three kinds of atomic and molecular linkages:

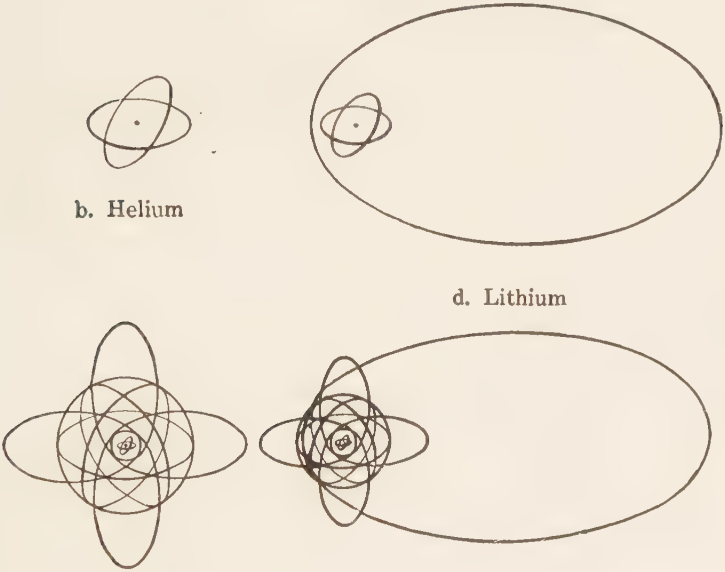
1. Polar or ionizable linkages between the oppositely charged ions of a salt.
2. Non-polar, non-ionizable linkages due to shared electrons.
3. The coördinate links of Werner (platinum chapter) capable of uniting apparently saturated molecules.

The Bohr Atom.—Bohr's conception of the atom, a conception that is changing under criticism, differs from the static arrangement of electrons suggested by G. N. Lewis and Langmuir. Bohr and the majority of physicists and chemists, at least in the year 1929, hold that the planetary electrons revolve at high velocities in circular and elliptical orbits around the nucleus. With the heavier atoms the arrangement of orbits is amazingly complicated and recently it has been suggested that the electrons are spinning as well as rotating around a nucleus and that the protons or nucleus also may be spinning.

In fact no present theory is without serious defects when used to explain chemical phenomena and forced to conform to all the mathematical laws of physics. The changing theories are at present the products of mathematics, physics, astronomy and chemistry. Well may we speak of the astronomy of the atom as more intricate than the astronomy of the heavens. Finally will come a stable theory, but just now we are suffering from "growing pains."

There is one distinct advantage in the modified Bohr theory worthy of mention here. By the Lewis and Langmuir theory no outer shell can be begun until the electron layers or shells beneath are complete. Not so with the Bohr theory which insists that although the outermost class (shell?) of orbits cannot contain *more* than 8 electrons and the next to the outermost cannot contain *more* than 18, there may, however, be fewer than 18 in this layer even while the outer layer contains one or more electrons.

By this plan the maximum number of planetary electrons in the atom (reading from the center outward) may be two or 2, 8 or 2, 8, 8 or 2, 8, 18, 8 or 2, 8, 18, 18, 8 or 2, 8, 18, 32, 18, 8. However, the variable valences of copper are explained by permissible variations in the placing of electrons in the two outer layers. In cuprous salts we find the arrangement 2, 8, 18, 1, while in cupric salts we find the arrangement 2, 8, 17, 2.



b. Helium

d. Lithium

c. Neon

e. Sodium

Fig. 87.—Electron orbits in Bohr atoms.

In chromates the element may have the 2, 8, 8, 6 electron plan and in chromous salts the 2, 8, 12, 2. Note that the outer valence electrons in the chromium of chromates number 6 and in chromous salts only 2, entirely in accord with the usual conception of their valence. (Explain it with copper.) Similarly, the valence and the color of manganese compounds may be explained.

Isotopes.—Soddy coined the word *isotopes* to describe two or more elements of different atomic weights, but with identical chemical properties. They have the same number and arrangement of planetary electrons but a different number of protons and electrons in the nucleus. By positive-ray analysis Aston found krypton

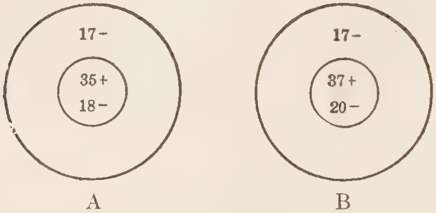


FIG. 88.—Chlorine isotopes. A, atomic weight 35; B, atomic weight 37.

TABLE OF ISOTOPES

ELEMENT	ATOMIC WEIGHT	MASSES OF ISOTOPES IN ORDER OF INTENSITY
Li	6.94	7: 6
B	10.9	11; 10
Ne	20.2	20; 22
Mg	24.32	24; 25; 26
Si	28.1	28; 29; 30
Cl	35.46	35; 37
Ar	39.9	40; 36
K	39.10	39; 41
Ca	40.07	40; 44
Fe	55.84	56; 54
Ni	58.68	58; 60
Cu	63.57	63; 65
Zn	65.37	64; 66; 68; 70
Ga	69.72	69; 71
Ge	72.38	74; 72; 70
Se	79.2	80; 78; 76; 82; 77; 74
Br	79.92	79; 81
Kr	82.92	84; 86; 82; 83; 80; 78
Rb	85.45	85; 87
Sr	87.63	88; 86
Zr	91	90; 94; 92; (96)
Ag	107.88	107; 109
Cd	112.41	114; 112; 110; 113; 111; 116
Sn	118.7	120; 118; 116; 124; 119; 117; 122; (121)
Sb	121.77	121; 123
Te	127.5	128; 130; 126
Xe	130.2	129; 132; 131; 134; 136; 128; 130; (126); (124)
Ba	137.37	138; (136)
Ce	140.25	140; 142
Nd	144.27	142; 144; 146; (145)
Hg	200.6	(197); 202; 204; 198; 199; 200

to have six isotopes with atomic weights of 78, 80, 82, 83, 84, and 86.

Harkins showed the existence of at least two chlorine isotopes of atomic weight 35 and 37 mixed in such proportions as to give the usual atomic weight of 35.46. Their chemical properties are the same because there are the same number of electrons in the outer shells.

Mercury and a number of other elements are really mixtures of isotopes. An example of isotopes recently discovered is found in the two kinds of antimony. Hungarian antimony has an atomic weight of 121.1 while Bolivian antimony has an atomic weight of 122.4. However, since all the parts of an isotopic mixture are alike chemically, there need be no confusion in our consideration of elements.

The atomic weight of any group of isotopes (usually referred to as a single chemical element) is really only the average of the different isotopes making up the mixture. No wonder our usual atomic weights include so many fractions.

Different elements of the same atomic mass are called *Isobares.* Some of the radioactive elements illustrate this. Isobares do not have the same chemical and physical properties, but are alike only in atomic mass. This is due to the fact that the arrangement of electrons in the nuclei and in the outer shells of the atoms are different.

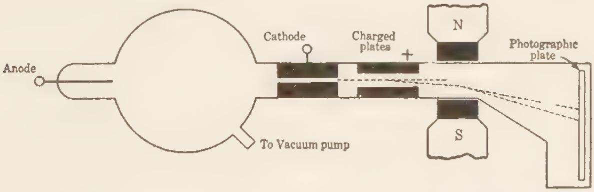


FIG. 89.

Positive Ray Analysis.—In Fig. 89 is represented a vacuum tube *O* with anode, and cathode perforated in the center. When a trace of some gas is admitted while a high potential electric discharge takes place the high-speed electrons from the cathode knock electrons out of the gas molecules, thus forming positively charged gas ions. Under the electric stress these positive gas ions are driven toward the cathode, through the small center hole, and on to the photographic plate. Under the influence of a powerful magnetic field and electrical field NS these positive rays are bent out of their straight-line course according to the charge (readily calculated), speed, and mass. Ions of equal mass are focused on the same line on the photographic plate, those of other masses on parallel lines. Hence it is possible to calculate, from the positions of these bands, relative masses of atoms. Aston, the English physicist, has so improved J. J. Thomson's original apparatus that his error in determining atomic weights is only one part in 1000.

When the rays come from a mixture of isotopes of an element, each isotope is marked by a separate band on the photographic plate. From the position of the bands the mass of the corresponding atom can be learned.

Change of Mass to Energy.—If the helium atom with a mass of exactly 4 is built up from four hydrogen atoms there must be a slight loss of mass in the close packing of nuclei since $4 \times 1.008 = 4.032$. If this theory is correct, and mass is converted into energy, the energy released by the sun corresponds to a loss of mass equal to 4,000,000 tons per second.

It is held by many that all atoms are built up from hydrogen and helium nuclei, those with atomic weights exactly divisible by 4 using only helium "bricks" and those with atomic weights not exact multiples of four (the elements of odd atomic weights) using both helium and hydrogen bricks.

The Hot-Cathode Tube.—Coolidge has made a powerful cathode tube using a small spiral of tungsten wire heated by an independent circuit as the source of slow-moving electrons. With a voltage of 350,000 to speed up the electrons (150,000 miles per second) and a marvellously thin nickel-foil window for emergence of these cathode rays, a new tool has been invented. Three tubes in series treble the effect. The effects of such an electron bombardment is as great as if one ton of radium had been used as a source of radiations. A metal target in the last tube of a series can give a powerful source of X-rays.

EXERCISES

5. What has become of the molecule in a crystal of common salt?
6. What is the difference between a proton and an electron?
7. What element has recently been discovered?

8. What is the difference between the simple cube, the face-centered cube, and the body-centered cube in crystal structure?

9. Compare the diffraction gratings used for invisible light with those used for X-rays.

10. What do the outer-shell electrons in an atom have to do with valence? What do they have to do with chemical reactions?

11. Why is the atom of argon so stable and so inert?

12. What is the difference between the electron processes in formation of CCl_4 and NaCl?

13. What is the unit in the crystal lattice of sugar?

14. What is the difference between the Bohr atom and the Lewis-Langmuir atom?

15. What started us on our way to the present conception of the atom?

16. Why doesn't carbon tetrachloride ionize?

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CHAPTER XXII

THE ATMOSPHERE. THE ARGON FAMILY

The Atmosphere

The earth is bathed in a great ocean of invisible gas called the atmosphere. From it animals and plants draw vast quantities of elements essential to their growth; on its motion we depend for much of our physical comfort and mental efficiency; and to its dust and moisture content we owe a great part of the natural beauty we enjoy. It carried sound, brings water from the ocean reservoir to thirsty fields, and has played a great rôle in history by driving ships across the seas.

Truly the atmosphere is worthy of study. Apparently so light that it scarcely impedes our movements yet it presses upon us with a weight of nearly 15 pounds per square inch. The air resting on a single acre of earth weighs over 40,000 tons.

At 21,000 feet elevation the air pressure is so low that airplane engines reach their limit (unless aided by a supercharger). Such rarefied air contains only half the sea-level amount of oxygen, hence the exhaust gases are directed against a turbine wheel which operates an air compressor designed to feed air at sea-level density into the engine. So aided, aviators have climbed seven miles, and found a "ceiling" temperature of − 60° C. (or − 76° F.). Even at 15,000 feet oxygen flasks must be connected with the aviators' helmets to aid breathing.

Air a Mixture.—About 99 per cent of air is composed of two gases, oxygen and nitrogen, and the proportions of these vary but slightly. Several other substances are present, some in proportions that vary considerably. The approximate composition of dry air is given below.

Nitrogen	78.00	per cent (Volume)
Oxygen	21.00	per cent (Volume)
Argon	0.933	per cent (Volume)
Carbon dioxide	0.03	per cent (Volume)
	99.963	

In addition to the four above named there are found water vapor, helium, neon, krypton, xenon, dust and sometimes ozone, hydrogen sulfide, and oxides of nitrogen in traces. Obviously the dust content varies with the wind and other factors, and water vapor may be present in excessive amounts in the jungle, or nearly lacking over the desert.

The evidence that these various constituents are present merely as a mixture and not as one compound is convincing.

1. Each constituent of the air retains its own properties irrespective of the presence of the others. The oxygen is just as soluble in water as if the nitrogen were missing.

2. The properties of air are the mean of the properties of its components, which is not true of a compound. The density, for example, is what might be calculated from such a mixture.

3. When liquid air evaporates, the more volatile nitrogen tends to escape faster than the oxygen. In pure compounds, water for example, the distillate has exactly the same composition as the original liquid, unless decomposition occurred. Therefore air can be separated into its constituents by liquefaction and fractional distillation. Compounds cannot.

4. Nitrogen and oxygen can be mixed in the same proportion as found in air, without change in temperature or volume, and yet produce a mixture like air. Evidently no reaction occurs.

5. The proportions by weight cannot be represented by a chemical formula because the constituent gases are not found in exact multiples of atomic weights. This alone is a clinching argument.

Exercise 1.—Why doesn't the oxygen, heavier than nitrogen, settle and the nitrogen rise?

The Oxygen Carbon Dioxide Balance.—It may seem alarming to learn that there are 2450 thousand million tons of carbon dioxide in the atmosphere, but this means only three parts in 10,000 of country air or twice that much in city air. We can live in air containing many times that amount of carbon dioxide.

This carbon dioxide has its source in the decay and fermentation of animal and plant bodies, in volcanic eruptions, in the respiration of animals and the combustion of fuel. The world burns over 1,300,000,000 tons of coal annually, but even so we would have to keep this up 600 years to double the present amount of carbon dioxide—if none were removed from the air. At every breath a man uses on an average 500 cc. of air and puts four per cent of carbon dioxide in it. At the same time animals are using oxygen to burn their worn-out tissues, and the combustion of fuel is consuming even more of this vital gas. Carbon dioxide even issues from the earth in some mineral springs.

We might look into the future with fear that robbing the atmosphere of oxygen and pouring carbon dioxide into it will finally make this globe uninhabitable. But fortunately nature maintains a beautiful balance. By the catalytic action of the green chlorophyll of leaves plants utilize atmospheric carbon dioxide as food; in fact, this gas is their only source of carbon. In past ages plants were converted into coal (largely carbon) and now we burn the same coal with evolution of carbon dioxide —and heat, fortunately. Thus the cycle of carbon in nature is repeated. Providence steps in here and puts the finish of perfection on the arrangement. In utilizing carbon dioxide the plant keeps all the carbon and rejects the oxygen, thus purifying the air.

But this is not the only safeguard. Carbon dioxide is soluble in water, so the quantity in the ocean is vastly greater than that in the atmosphere. Shell-fish take up immense amounts for their shells (calcium carbonate).

Dust.—One of the variable components of air is dust, part of the time a nuisance and all the time a blessing. Each raindrop forms around a particle of dust as a nucleus and, for that matter, so does each minute water drop of a cloud or mist. Ionized gases also furnish nuclei, but the influence of dust is probably greater. It is estimated that in a storm of March 9, 1918, one million tons of dust was carried 1000 miles from the southwestern United States into the Mississippi Valley. The volcanic eruption of Krakatoa in 1883 left dust in the air on the opposite side of the earth for three years causing magnificent red sunsets. London air contains 10,000 dust particles per cubic centimeter, their best "pea soup" fog, 50,000.

Without dust (or gaseous ions) we should have no rain. On cooling, air would become supersaturated and a distressingly heavy dew would cover our faces, clothing, houses, and the earth surface generally. We should have no soft haze to lend enchantment to distance, no twilight, no glorious sunset glows, and no beautiful clouds.

Humidity.—Air can take up water vapor until the partial pressure of the water vapor equals the vapor pressure of water at that particular temperature. The humidity is then 100 per cent and the air is saturated with moisture. The student may recall that in collecting gases over water the inclosed gas had a good opportunity to become saturated. This condition is not so common in outdoor air which, although in contact with lakes, rivers, and oceans, is so stirred by winds that its humidity reaches 100 per cent only when cooled sufficiently.

Air saturated at 20° has a vapor pressure of 17.5 mm. If the total pressure of the air is 750 mm., then $\frac{17.5}{750.0}$ or about 2.3 per cent of it is due to water vapor. In other words, about 2.33 per cent of the air under those conditions is water vapor. Of course each constituent gas occupies the entire volume.

EXERCISE 2.—What would be the weight of water in 500 cubic meters of air saturated at 23° and under a pressure of 760 mm.? Remember the use of the G. M. V.

On cooling this air to 10° the vapor pressure becomes only 9.18 mm., so the water vapor then occupies only about 1.22 per cent of the volume of the air, or it would if only the water vapor were present and the pressure were kept the same. The difference between this and the amount held at 20° was precipitated as dew, fog, or rain.

If, however, air saturated at 10° is warmed to 20°, it is no longer saturated, that is, if it is not in actual contact with a body of water. Its vapor pressure is still only 9.18 mm., while air at 20° is capable of holding nearly twice as much moisture. The humidity is not 100 per cent, but $\frac{9.18}{17.5}$, or 52.5 per cent.

The humidity of outdoor air in temperate climates averages about 66 per cent, although the seasonal variations may be great. Moist air is lighter than dry air, although it feels "heavy." The mean molecular weight of the nitrogen and oxygen in air is 28.955, but the molecular weight of water as a gas is only 18. The most comfortable humidity of air is from 50 to 60 per cent. However, in winter it is almost impossible to maintain this condition in our houses. With zero weather outside and 68° F. within, the evaporation of 30 gallons of water daily would be required in order to maintain a relative humidity of 40 in a large house. With freezing weather outdoors the evaporation requirement would be only 7 gallons.

Comfort demands a rise in temperature when the humidity falls.

Sadtler states that one cubic mile of air saturated at 35° C. (95° F.) would throw down a flood of 140,000 tons of water if suddenly cooled to freezing.

Ventilation.—The old idea of correct ventilation was that the accumulation of carbon dioxide and the loss of oxygen must be prevented by introducing fresh air. The general effect was good, but not for the reasons formerly given. Carbon dioxide is not a poison and 400 parts of this gas in 10,000 parts of air (as compared with the usual 4 to 6 in 10,000) can be breathed without discomfort. Nor is a considerable reduction in the amount of oxygen such a desperate matter as was once thought. We are accustomed to an atmosphere containing about 21 per cent oxygen, yet air containing only 10 per cent will sustain life.

All agree now that the humidity of the air next the skin is an important factor in ventilation. The temperature of the human body is regulated to 98.6 F. by evaporation of perspiration. Evaporation of 14 g. of water cools an average man more than 0.1° C. (or half an ounce loss lowers the temperature about 0.2° F.). The evaporation of one quart removes 500 calories. Nature regulates the evaporation to suit our needs. Now the layer of air in contact with the skin quickly becomes saturated and evaporation is checked unless fresh, dry air replaces this layer. Such replacement is effected by gentle air currents set up in our efforts to introduce outdoor air. Even a fan stirring the same old air produces greater comfort, although when all the stale air becomes saturated by evaporation no further relief can be secured by this device. Thus the ancient practice of bringing in fresh air is right, largely because the humidity is thus kept down, although there can be no doubt that we thrive better on an atmosphere of 21 per cent oxygen than on one not so rich. We must not go to the other extreme and reason that very dry air should be most comfortable. If too dry, the air takes up moisture from the delicate mucous membranes of mouth, throat, and nose at a rate that overworks them, with consequent danger from catarrh.

Modern ventilation engineers arrange for 2000 cubic feet of fresh air per hour for each person. In many great auditoriums the entire body of air is changed every ten or fifteen minutes. Opening windows is not always possible because of noise, dust, or direct drafts; so ventilating fans, both blowers and exhaust fans, are resorted to. The best practice to-day calls for blowing the fresh air through a spray of water to wash out dust and introduce enough (but not too much) moisture. In removing most of the dust the bacteria are also largely removed. It is interesting to know that to humidify the average house in winter the evaporation of several gallons of water per day is required.

Liquid Air.—The liquefaction of air is an industry of considerable importance because it is the first step in securing oxygen and nitrogen for other industries. To liquefy the air it is first freed from carbon dioxide by washing with water and passing over lime. The air is then subjected to high pressure, the heat of compression at 200 atmospheres being removed by cooling with running water. Under such high pressure and slightly lowered temperature the moisture in the gas is condensed. The last traces of water and carbon dioxide are absorbed by sodium hydroxide. The liquefier proper (Fig. 90) is nothing but a coil of very small copper tube with a valve to control the flow of air. The coil is contained in a metal jacket which is heat-insulated with wool. On opening the valve the compressed air expands as it escapes. This cools it somewhat. It is then made to travel back through the jacket, thus further cooling the air in the copper tube. After a few minutes this progressive cooling produces a steady stream of liquid air.

To keep the air, use is made of a device invented by Dewar (Fig. 91). He made a double-walled flask and evacuated the space between the two walls. A vacuum is a very poor conductor of heat. The inside walls were silvered also to reflect radiant heat. A cork stopper, loosely fitting, aided in heat insulation. Dewar found such flasks kept liquid air a surprising length of time. We use similar containers, to keep liquids hot or cold, under such names as "Thermos" bottles.

Liquid air boils at − 194° to − 185° according to its composition. Since the nitrogen tends to evaporate first there is a steady change in composition and boiling point. Since the critical temperature is − 140°, it cannot be liquefied above this temperature and at − 140° about 39 atmospheres pressure are necessary to liquefy it. At lower temperatures much lower pressures suffice.

Fresh liquid air is almost colorless, but as the nitrogen escapes the bluish tint of oxygen appears. The liquid when fresh is lighter than water. Startling experiments can be performed with this liquid. In contact with it chlorine, hydrogen chloride, methane, ammonia, hydrogen sulfide, and some other gases freeze to odorless liquids. Even alcohol and kerosene are persuaded to freeze by its magic touch. Metals lose much of their electrical resistance in liquid air.

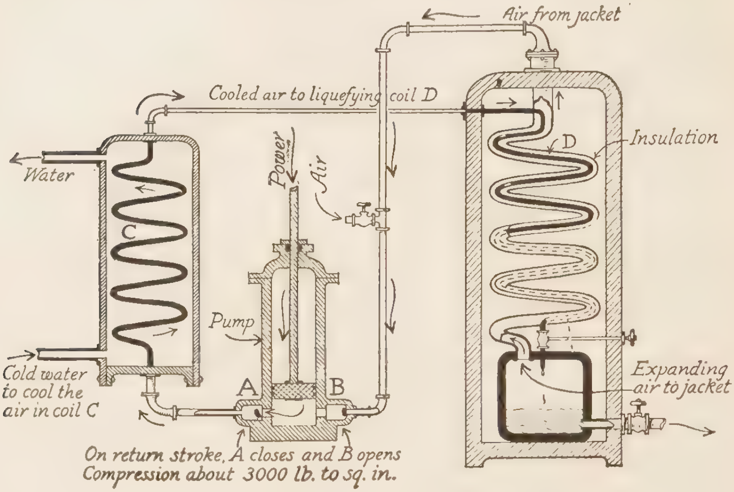
Air from jacket
Cooled air to liquefying coil D
Insulation
D
Water
C
Power
Air
Pump
Cold water to cool the air in coil C
A
B
Expanding air to jacket
On return stroke, A closes and B opens
Compression about 3000 lb. to sq. in.

Fig. 90.—Liquid air apparatus.

The liquid oxygen left after escape of the nitrogen can be used to make high explosives (for immediate use). Charcoal wet with the proper amount of liquid oxygen explodes with the violence of dynamite if set off by a fulminating cap.

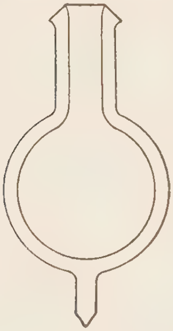

Fig. 91.—Dewar bulb, the first thermos bottle.

Exercise 3.—Why remove carbon dioxide and water vapor before liquefying air?

The Liquefaction of Gases.—Faraday was the father of commercial gas liquefaction. He used a combination of low temperature and high pressure. With a mixture of solid carbon dioxide and ether he secured a temperature of − 80°. In 1845 Faraday had liquefied all known gases except five—hydrogen, nitrogen, oxygen, nitrous oxide, and carbon monoxide—the so-called "permanent gases." In 1869 Andrews showed that for every gas there is a temperature above which it cannot be liquefied. Therefore low temperatures were the necessary factor. The truth was that Faraday failed to get those five gases cold enough.

FIG. 92.—Liquid air plant at Muscle Shoals.

Even in later years scientists could not liquefy hydrogen at − 190°. Dewar proceeded in 1898 to compress hydrogen, chill it to about − 185° with liquid air, and then let the hydrogen expand. This expansion lowered the temperature below − 243°, its critical temperature. Under these conditions only 11 atmospheres pressure were required to liquefy it. The contraction in volume on liquefaction of a gas is, in general, very great. One liter of carbon dioxide as measured at 0° and 760 mm. pressure yields only 2 cc. of liquid when sufficiently compressed.

The Joule-Thomson effect, or cooling due to internal work against the mutual attraction of molecules, makes possible the liquefaction of gases by expansion of the highly compressed and precooled gas from a nozzle. This effect increases as the temperature falls. Hence, to liquefy hydrogen (for which the Joule-Thomson effect is generally negative) it is necessary to cool first with liquid air.

About 1907 the development of the liquid air industry gave a great impetus to the manufacture of oxygen, and this in turn created a demand for compressed (not liquefied) hydrogen and acetylene for blowpipe work. The annual production of liquefied or highly compressed gases in the United States is worth $40,000,000. Oxygen leads, followed by acetylene, carbon dioxide, ammonia, chlorine, nitrous oxide, and hydrogen. It is inspiring to read the splendid chapter on this subject in the *Encyclopœdia Britannica* (Liquefaction of Gases).

EXERCISE 4.—Read the popular account of Onnes' low-temperature work in *Harper's Magazine* (Vol. 129, page 783, 1914) and report briefly

THE ARGON FAMILY

Argon.—The fulfillment of prophecy is not confined to the Scriptures. Chemistry offers many examples. Back in 1785 Cavendish passed electric sparks through air, making the oxygen and nitrogen unite to form oxides of nitrogen, which he removed by reaction with a base. Excess oxygen was added to provide enough for all the nitrogen. Yet after removal of all the gases Cavendish could think of there was a little gas left, about 1/120 of the original volume. His partial discovery lay unused for over a century, yet it was really a sort of prediction that a new gas would some day be found in the air.

In 1895 the great English physicist, Lord Rayleigh, observed that apparently pure nitrogen made by removing everything else from air (as by Cavendish's method) was distinctly heavier than the unquestionably pure nitrogen made by decomposing ammonium nitrite. Calling in the chemist, Sir William Ramsay, to help, Rayleigh proceeded to pass the "atmospheric" nitrogen over hot magnesium, which unites with nitrogen. They found a gas left over, evidently the same residue that puzzled Cavendish, for its volume was not far from 1/120 that of the original air. Because it was chemically inert, they named the new element with the Greek word for "lazy," argon.

Ramsay used liquid air as a source of argon and found the last portions on evaporation rich in argon. This gas makes up 0.933 per cent of the air by volume. It is also found in some mineral waters, in fire damp, and in some volcanic gases. Since it is so inactive it has no compounds. Millions of tungsten lamps are now filled with argon because by the use of this gas greater brilliance and longer life can be secured.

Read Rayleigh's own story of "Argon" in the *Encyclopædia Britannica.*

Helium.—The American chemist Hillebrand made a chance observation in 1889 that the uranium mineral, uraninite, on treatment with acids released a rather inactive gas (which he supposed was nitrogen). Years later Ramsay, in search of new sources of two rare gases, repeated Hillebrand's experiment, using the mineral cleveite, and secured a very inert gas different from any element then known. He found its spectrum identical with that of an element observed in the sun by Lockyer and Janssen during the solar eclipse of 1868.

They had called it helium (from the Greek, "helios," the sun). Rather astonishing to discover our new elements in the sun by lines in the solar spectrum and long afterwards to find the distant element right on our own doorstep. Soon afterward Ramsay isolated helium from the first fractions of liquid air.

Helium is so inactive that it has no compounds. It boiled at 5.1° above absolute zero, when first liquefied by Onnes in 1908. This was the only gas left to conquer, so Onnes completed the brilliant work on liquefaction begun so well by Faraday when he liquefied chlorine in 1823. By the rapid evaporation of liquid helium Onnes secured a temperature within 0.82° of absolute zero. In 1926 Keesom, Onnes' successor at the University of Leiden, froze helium to a solid at a temperature of about 1° Abs. and at a pressure of 28 atmospheres. It is an interesting fact that helium conducts heat six times as well as air. The spark gap in helium is ten times as long as that in oxygen.

The romance of helium makes one of the best chapters in modern chemistry. It is closely related to the magic of radium, for every radium compound is continually releasing helium, a most astounding fact. Radium is an element in the sense that man cannot decompose it by any effort on his part. However, it is decomposing spontaneously into helium and other products.

By measuring the rate of formation we are able to calculate how long it has taken the mineral fergusonite to accumulate the helium it contains. Such a calculation indicates 26,000,000 years as the age of fergusonite.

During the Great War Ramsay suggested that airships and balloons should be lifted by helium instead of hydrogen. Hydrogen, although plentiful and cheap, has its drawbacks. Flaming bullets or atmospheric electricity have ignited hydrogen balloons, but helium refuses to burn. Although its density is twice as great as the density of hydrogen, its lifting power is 92 per cent as great. Lifting power is measured by the difference in weight of the helium (or hydrogen) and air. A mixture of 80 per cent helium and 20 per cent hydrogen is non-inflammable.

Ramsay's suggestion lacked only one thing—the helium. He died at the height of the war, while still searching for a commercial source. Yet Cady, the American chemist, had previously found as much as 1.84 per cent helium in Kansas natural gas. Moore, who had worked with Ramsay, brought this neglected fact to the attention of our Chemical Warfare Service and ingenious methods were at once applied in an effort to separate helium from the natural gas. The Petrolia field of Texas, with gas yielding nearly 1 per cent helium, was selected as most suitable. Just as the war closed we had commercial plants in actual operation and 150,000 cubic feet in cylinders on the New Orleans docks ready for shipment to Europe. Thus American scientists added another achievement to their long list of military scientific successes.

The United States is fortunate in owning the most workable sources of helium. Canadian gas contains about 0.36 per cent, but no other country has any source worthy of mention. A Colorado well in 1929 yielded natural gas containing 6 per cent helium. Before the war, very little helium had been secured and the cost was appalling—nearly $2000 per cubic foot. At this price our first shipment was worth $300,000,000 but the present cost is only two or three cents per cubic foot.

In 1929 United States helium plants reached a capacity of 23,000,000 cubic feet per year. The gas is stored in cylinders holding 200 cubic feet at 1800 lbs. pressure. The new U. S. Navy airships will require 6,500,000 cubic feet for a filling and there is a loss by diffusion.

The United States Army Air Service now has a helium purification plant. When a helium balloon no longer rises because of the diffusion of air into the ballon the mixture of gases can be chilled to extremely low temperatures and passed over "activated" charcoal. The other gases are absorbed but the helium is not. It is then condensed in cylinders ready for use again. Helium has the lowest boiling point known, − 267.9° C.. and the lowest water solubility of any gas known.

It is possible to avoid the "bends," as divers and tunnel workers call the dangerous condition produced when they are brought too swiftly out of high-pressure depths by diluting oxygen in a diver's breathing atmosphere with inert helium instead of nitrogen. Unfortunately nitrogen forms bubbles in the blood stream as atmospheric pressure is reduced rapidly because the nitrogen does not escape rapidly enough from the solution. Helium escapes from blood solution far more swiftly with but little bubble hazard.

Although helium is now secured from certain natural gas wells, it may possibly be obtained from air when the cost is sufficiently reduced. At many miles distance above the earth it is supposed that the atmosphere is largely helium and hydrogen, the two lightest gases.

Krypton, Xenon, and Neon.—After the discovery of argon and helium it was apparent that there must be three or four unknown elements in the same family in order to round out the periodic table. With this incentive Ramsay carefully fractionated liquid air and obtained neon (Ne), krypton (Kr), and xenon (X). These "rare gases," and they are truly rare, since only traces are found in the atmosphere, are quite inactive, like argon and helium.

The Air Separation Industry.—In 1900 the separated constituents of the air had but little commercial significance, while now the value of plants and equipment for separating, handling, and using these gases is over $300,000,000.00.

Nitrogen		78.03% by volume
Oxygen		20.99% " "
Argon		0.94% " "
Hydrogen	1 part in	8,000
Neon	1 " "	80,000
Helium	1 " "	250,000
Krypton	1 " "	1,000,000
Xenon	1 " "	11,000,000

Composition of the atmosphere (omitting compounds, such as CO_2 and H_2O and dust).

The use of ***neon-filled glass tubes*** for advertising signs and for fog beacons is comparatively recent. The tubes are really almost vacuum tubes containing neon at the very low pressure of five to ten millimeters. The rarefied gas glows with a marvellously penetrating red light when an alternating electric current is passed through at 8,000–10,000 volts and 15–25 milliamperes (60 cycles). With a little added mercury vapor in a fluorescent greenish tube a good green color is produced. A proper proportion of neon light (low in the spectrum) and mercury vapor light (high in the spectrum) gives an approximation to white light useful in photography. The penetrating quality of neon light through fogs (because of low refraction of red light) makes it valuable in marking airplane landing fields and harbors.

An ordinary electric bulb sign on top of an Akron building was replaced by neon tubes. Only one-seventh as much electricity was needed while the sign was visible at seven times the previous distance.

EXERCISES

5. How could the General Electric Company secure argon from air for its tungsten lamp? Do you think oxygen would serve as well as argon in the lamps?
6. Why don't we gradually use up all the oxygen of the air and replace it with carbon dioxide?
7. Why is helium a valuable material resource? How do we know it is found in the sun?

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"Detailed Story of the Discovery of Helium in Natural Gas," *J. Chem. Ed.*, *3*, 47, (1926).

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CHAPTER XXIII

EQUILIBRIUM

On page 79 the reversible reaction

$$(1)\quad Fe_3O_4 + 4\ H_2 \rightleftarrows 3\ Fe + 4\ H_2O$$

was discussed as an example of chemical equilibrium. Another reversible reaction mentioned as of great importance was the following:

$$(2)\quad Cl_2 + H_2O \rightleftarrows HCl + HOCl.$$

In connection with the latter reaction it was stated that in the sunlight the hypochlorous acid decomposes so that the equilibrium is steadily disturbed towards the right. Naturally if the hypochlorous acid were no longer present it could not react with the hydrochloric acid to form any more chlorine and water. In other words, removal of one product disturbs equilibrium in the direction favoring formation of more of that product. The same result is achieved by addition of a base, which, of course, neutralizes the acids, thus suppressing completely any reaction to the left.

It has been stated that escape of a product as a gas prevents reversion of a reaction and so such reactions proceed to completion. This may occur quite simply, as in the attack of an acid on a metal or on a carbonate:

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow,$$
$$CaCO_3 + 2\ HCl \longrightarrow CaCl_2 + H_2O + CO_2\uparrow.$$

To be exact, there are some reactions which would not be reversed even if the escape of a gas were prevented by suitable means. There must be some affinity (tendency to react) between the products or no reaction occurs.

In equation (1) this removal of one product as a gas may be brought about if the iron oxide is heated in a tube open at both ends while a stream of hydrogen is passed through. This hydrogen stream steadily removes water as fast as formed and the equilibrium, such as might exist in a closed tube, is continuously disturbed to the right. The student should read again the discussion of this reaction on page 79. Another device to secure the removal of one product as a gas is to heat to a suitable temperature. For example, nitric acid is often prepared by heating a mixture of concentrated sulfuric acid and sodium nitrate. Care is taken to heat only above the boiling point of the nitric acid but not above the boiling point of sulfuric acid:

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3 \uparrow .$$

On page 175 the preparation of hydrogen chloride from concentrated sulfuric acid and sodium chloride is described. The hydrogen chloride escapes because it is insoluble in concentrated sulfuric acid:

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl \uparrow .$$

However, if dilute sulfuric acid is used, no gas escapes, even on warming. The great solubility of hydrogen chloride in water keeps it in contact with the sodium hydrogen sulfate and reaction follows. Thus an equilibrium involving four substances results.

$$NaCl + H_2SO_4 \rightleftarrows NaHSO_4 + HCl.$$

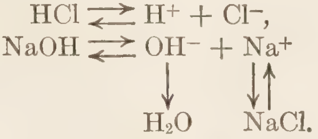
All ionization reactions involve equilibria which may be disturbed in one direction or the other by dilution or concentration:

$$NaCl \rightleftarrows Na^+ + Cl^-.$$

Here again such reactions may be made to proceed to completion by removal of one of the products. This could be accomplished very simply in the case of sodium chloride by addition of any positive ion capable of uniting with the chloride ion to form an insoluble compound. Silver ion (from a solution of silver nitrate, for example) unites with chloride ion, forming insoluble silver chloride, and thus forces complete progressive ionization of all the sodium chloride molecules:

$$\begin{tikzcd}[row sep=small, column sep=tiny]
NaCl \rightleftarrows & Na^+ & + & Cl^-, \\
AgNO_3 \rightleftarrows & NO_3^- \arrow[d, shift right] & + & Ag^+ \arrow[d] \\
& NaNO_3 \arrow[u, shift right] & & AgCl.
\end{tikzcd}$$

It is not always necessary even to remove an ion in the form of a precipitate or a gas. It may possibly react with another ion to form a slightly ionized substance, such as water, or a weak acid or base.



$$\begin{array}{rcccc} \mathrm{HCl} & \rightleftarrows & \mathrm{H^+} & + & \mathrm{Cl^-}, \\ \mathrm{NaOH} & \rightleftarrows & \mathrm{OH^-} & + & \mathrm{Na^+} \\ & & \downarrow & & \downarrow\uparrow \\ & & \mathrm{H_2O} & & \mathrm{NaCl}. \end{array}$$

The neutralization of an acid by a base, as outlined above, is not a reaction between molecules but between ions. The removal of H^+ ion and OH^- ion from the solution forces the complete ionization of all molecules of the original substance.

EXERCISE 1.—Give an illustration showing how an ionic equilibrium can be disturbed by tying up one of the ions in molecules of a weak acid or a weak base.

EXERCISE 2.—The preparation of a pure compound by double decomposition depends upon a choice of reacting ions such that the reaction shall proceed to completion or nearly so. Give examples of different ways in which this may be done.

Since any positive ion attracts and discharges any negative ion, there is no question of any lack of chemical affinity when solutions of electrolytes are mixed.

Two types of equilibrium are shown in Fig. 93 a reaction equilibrium and a solution equilibrium. If the bottle is only partly filled, NH_3 escapes into the air space until the velocity of return of NH_3 molecules equals that of escape when an equilibrium results. If the stopper is removed, NH_3 molecules wander away without adequate return, thus disturbing the solution equilibrium. The loss of more dissolved NH_3 disturbs the reaction equilibrium and finally nothing but water is left in the bottle.

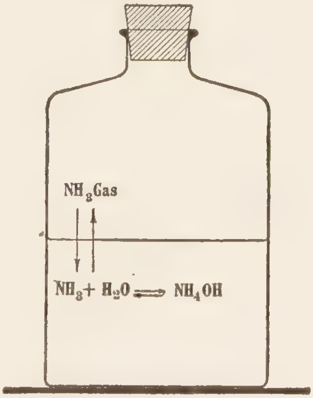


FIG. 93.—Two examples of equilibrium.

EXERCISE 3.—What would happen if into a bottle half filled with ammonia water an excess of acid were added and the stopper quickly replaced?

EXERCISE 4.—Iodine water is shaken with carbon disulfide. Then a base is added with shaking. Explain why the carbon disulfide becomes colorless.

Effect of Change in Temperature.—All reactions increase in speed with rise in temperature, but such increase is not the same in all cases. Thus one reaction in an equilibrium condition may be accelerated more than the opposing reaction. As a result the equilibrium would be disturbed and a new adjustment of velocities reached. That reaction will be favored which absorbs heat. "With rise in temperature an equilibrium is disturbed in the direction which absorbs heat" (Van't Hoff's Law). For example: Deacon's obsolete process of making chlorine from hydrogen chloride works best at a moderate temperature.

$$(1)\ 4\ HCl + O_2 \rightleftarrows 2\ H_2O + 2\ Cl_2 + 28{,}000\ \text{cal.}$$

A rise in temperature disturbs the existing equilibrium to the left. Of course some heating is necessary to secure sufficient velocity of reaction.

Effect of Change in Pressure.—Any increase in pressure on a system in equilibrium tends to bring reacting particles in closer contact and to compress the products. Consequently the formation of substances occupying a smaller volume will be favored. For example, one volume of nitrogen reacts with three volumes of hydrogen to form only two volumes of ammonia:

$$N_2 + H_2 + H_2 + H_2 \rightleftarrows 2\ NH_3.$$

In Haber's process great pressure is applied because pressure favors the formation of two volumes of ammonia from a total of four volumes of nitrogen and hydrogen. It goes without saying that high pressure must oppose the expansion involved in the decomposition of ammonia into its elements. This is another application of the Principle of Le Chatelier.

"When a stress is applied to a condition in equilibrium that reaction is favored which tends to undo the stress."

Effect of a Catalyst.—The effect of a catalyst is merely to bring about equilibrium more quickly. This is commercially important, for some opposing reactions do not come to a definite equilibrium for months unless hurried by a catalyst. If a catalyst could really disturb an existing equilibrium, it would be possible to get work done without any expenditure of energy by alternately removing and putting back the catalyst—a scientific impossibility.

The Law of Mass Action.—The speed of a reaction is proportional to the molecular concentration of the reacting substances and is also influenced by the nature of the molecules involved. (By a concentration of "1" we mean one gram-molecular weight per liter.) With solids and homogeneous liquids such concentration changes are not to be expected as with gases and substances in solution. Consider a reaction between two gases, A and B, in equilibrium with C and D:

$$A + B \rightleftarrows C + D.$$

Suppose we have, in a unit volume, just 1,000,000 molecules of A and an equal number of B. At a given temperature, etc., the speed of reaction to the right will be definite. But if we double the concentration of A, use 2,000,000 molecules per unit volume without changing B, it is obvious that the speed of reaction will be doubled because there will be just twice as many contacts per second between A and B as before. If we treble the concentration of B, take 3,000,000 molecules per unit volume, the previous speed of reaction must be trebled, due to three times as many contacts per second as before. The final speed must be six times the original speed since it was once doubled and that speed immediately trebled.

The same facts may be expressed in another way. Let the molecular concentration of A (number of gram-molecular weights per liter) be represented by [A] and the molecular concentration of B by [B]. Since the velocity of reaction is proportional to the concentration of A and also of B, it must be proportional to their product:

$$[A] \times [B] \propto \text{speed}.$$

Now it isn't really true that the number represented by this product equals the number of gram-molecular weights of C and D formed per second (the speed). We merely mean to say that the speed changes proportionately to any change in this product. We should, however, be justified in introducing a factor peculiar to the reaction, letting it represent all the other influences affecting a reaction. [A] × [B] represents the concentration influence only, but we must remember that temperature, affinity, and catalysis have an effect. Combine all but the concentration influence in *k*, which remains constant during any changes in concentration:

$$[A] \times [B] \times k = \text{speed}.$$

The speed of reaction between hydrogen and iodine is represented in exactly the same way:

$$[H_2] \times [I_2] \times k = \text{speed}.$$

It is not so simple in the case of the reaction between hydrogen and oxygen. We can approach this question by imagining three reacting substances, A, B, and C:

$$[A] \times [B] \times [C] \times k = \text{speed}.$$

Suppose B to be identical with A. Then the statement becomes

$$[A] \times [A] \times [C] \times k = \text{speed},$$

or

$$[A]^2 \times [C] \times k = \text{speed}.$$

Applying this logic to the reaction between hydrogen and oxygen we may write the following:

$$H_2 + H_2 + O_2 \longrightarrow 2\ H_2O,$$
$$[H_2] \times [H_2] \times [O_2] \times k = \text{speed},$$
$$[H_2]^2 \times [O_2] \times k = \text{speed}.$$

Application to an Equilibrium Reaction.—Let us assume that the reaction discussed is reversible:

$$A + B \rightleftarrows C + D.$$

Without further discussion it is evident that the speed of reaction to the left is proportional to the molecular concentration of C and D, and to a constant factor k' peculiar to that reaction:

$$\text{speed} = [C] \times [D] \times k'.$$

When equilibrium is reached the two speeds are equal:

$$[A] \times [B] \times k = [C] \times [D] \times k'.$$

By a simple algebraic process we may transform this into a more useful statement:

$$\frac{[A] \times [B]}{[C] \times [D]} = \frac{k'}{k} = K.$$

Since both k and k' were constant factors, despite the changes in concentration, the quotient $\frac{k'}{k}$ must also be a constant value represented by K. The convenient phrase "equilibrium constant" is applied to K.

An illustration of the application of the equilibrium constant may be found in the conditions in chlorine water:

$$\begin{aligned} Cl_2 + H_2O &\rightleftarrows HCl + HOCl, \\ [Cl_2] \times [H_2O] \times k &= \text{speed to right}, \\ \text{Speed to left} &= [HCl] \times [HOCl] \times k', \\ [Cl_2] \times [H_2O] \times k &= [HCl] \times [HOCl] \times k', \\ \frac{[Cl_2] \times [H_2O]}{[HCl] \times [HOCl]} &= K. \end{aligned}$$

Applications to Ionic Equilibrium.—It is very interesting to formulate and compare equilibrium constants for acids and bases. Here we begin to see some reason for the preceding drill. In the case of ions a molecular concentration of "1" means the weight of the ion in grams per liter. Since the SO_4 ion weighs 96, there should be 96 grams of this ion per liter to give a molecular concentration of 1. Consider a typical strong acid, such as hydrochloric, and a typical weak acid, such as acetic:

$$\begin{aligned} &HCl \rightleftarrows H^+ + Cl^-, \\ &\frac{[H^+] \times [Cl^-]}{[HCl]} = K, \\ &H \cdot C_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-, \\ &\frac{[H^+] \times [C_2H_3O_2^-]}{[H \cdot C_2H_3O_2]} = K'. \end{aligned}$$

The equilibrium (or ionization) constant, K, for hydrochloric acid is relatively much greater than the similar constant K', of an acetic acid solution of equal concentration. Strong acids are highly ionized in dilute solution so the numerator in such a fraction as $\frac{[H^+] \times [Cl^-]}{[HCl]}$ is much larger than the denominator. In a 0.1 N solution of hydrochloric acid only 8 per cent of the acid is present in the form of molecules, and consequently the molecular concentration of the ions is about 12 times as great as the figure for the molecules. In 0.1 N solution of acetic acid over 98 per cent of the molecules are not ionized, so the molecular concentration of acetic acid is over 49 times as great as the concentration of its ions. From this comparison we learn that K for weak acids is a very small number and for strong acids is relatively large. A similar statement holds for bases.

To calculate the ionization constant for an electrolyte we need only measure by suitable means the percentage of ionization and substitute the proper values in the formula. In a 0.1 N solution of hydrochloric acid the molecular concentration of HCl would be 0.1 if none of the molecules were ionized. However, only 8 per cent of this concentration remains in molecular form. (See page 214.) From all HCl molecules ionized there comes an equal number of H^+ ions and Cl^- ions. Thus the molecular concentration of the H^+ ions or the Cl^- ions must be $0.92 \times 0.1 = 0.092$ and the molecular concentration of the non-ionized molecules must be $0.08 \times 0.1 = .008$. Substituting these values we find K to be about 1, as it is for all strong acids and bases.

$$\frac{[H^+] \times [Cl^-]}{[HCl]} = K \quad \text{or} \quad \frac{[0.092] \times [0.092]}{[0.008]} = 1.058.$$

At other concentrations this value of K varies widely, so it is incorrect to speak of a *constant* value of K for *well-ionized* electrolytes. The ionization constant for acetic acid is only 1.8×10^{-5}, and for hydrocyanic acid (HCN) it is 7×10^{-10}. For all weak acids and bases the value of K is constant but it is very decidedly not a constant value for strong electrolytes.

Effect of Dilution.—Suppose a molar solution of an acid AB is exactly 10 per cent ionized. The concentration of the non-ionized molecules must be 0.9 and the concentration of each ion also 0.1. Substituting in the formula, we get the value 0.11 for K.

$$\frac{[0.1] \times [0.1]}{[0.9]} = \frac{0.01}{0.9} = 0.011.$$

On addition of an equal volume of water the concentrations must all be halved, if no further ionization occurred:

$$\frac{[0.05] \times [0.05]}{[0.45]} = \frac{0.0025}{0.45} = 0.00555.$$

But with increasing dilution a greater percentage of the molecules ionize, thus decreasing the numerical value of the denominator and increasing the value of the numerator. This adjustment is found, by actual laboratory observation, to be such that the value of the fraction for all except strong electrolytes remains constant, at 0.011 for K. Dilution does not change the ionization constant.

Effect of a Common Ion.—Acetic acid is a weak acid but more than sufficiently ionized to turn methyl orange red. If to such a red solution considerable sodium acetate is added, the color changes to yellow, indicating a great suppression of H^+ ion:

$$\frac{[H^+] \times [C_2H_3O_2^-]}{[H \cdot C_2H_3O_2]} = K.$$

Sodium acetate, like all soluble salts, ionizes very well, but acetic acid yields relatively few ions. Addition of much sodium acetate, therefore, greatly increases the concentration of the acetate ion in the equilibrium for acetic acid. Apparently this must increase the numerical value of the numerator in the above fraction, yet actual laboratory measurements show that K has not changed. The explanation is simple: any increase in the concentration of acetate ions affords more opportunities for contact with hydrogen ions, thus decreasing the concentration of hydrogen ions since they are tied up to some extent in the molecules of acetic acid thus formed. Suppose the concentration of acetate ions were increased 100 times. We might conclude that the concentration of hydrogen ions must be decreased to one hundredth of its previous value, but the value of $[H \cdot C_2H_3O_2]$ is also increasing. The fact is, all values adjust themselves so as to maintain K as a constant. Addition of potassium acetate would suppress the ionization of acetic acid in the same way.

However, an attempt to suppress the ionization of a strong acid like hydrochloric by addition of sodium chloride doesn't amount to much. The principle applies but there are too many hydrogen ions to suppress readily.

Precipitation Conditions.—In a *saturated* solution of any salt the concentration of the dissolved molecules must itself be a constant value. Otherwise more solid would dissolve or a precipitate would form and the solution could not have been saturated. Therefore, the variable [dissolved molecules] becomes a constant value and may be joined to the ionization constant.

The expression, $\frac{[Na^+] \times [Cl^-]}{[NaCl]} = K'$, for an unsaturated solu-

S. P. = the multiplication of ion concentrations
in a saturated solution.
moles per liter is grams mol wt per liter

tion, becomes $\frac{[Na^+] \times [Cl^-]}{k} = K'$ for a saturated solution. By an algebraic process this changes to a simpler form:

$$[Na^+] \times [Cl^-] = K' \times k = K.$$

For very soluble electrolytes this value, K, must be relatively large. For an insoluble salt like barium sulfate, K must be minute, since in a saturated solution of barium sulfate (1 g. per 400,000 cc.) there are too few Ba^{++} ions or SO_4^{--} ions to yield an ion product as large as K for sodium chloride. Evidently the value of K for saturated solutions is a direct measure of solubility, hence the name ***solubility product.*** To secure precipitation we need only increase the concentration of either ion (or of both) concerned to such a point that the product shall exceed K for a saturated solution of that electrolyte.

Sodium chloride is reasonably soluble and yet if into a saturated solution of that salt some hydrogen chloride gas is passed, crystals of sodium chloride settle out:

$$[Na^+] \times [Cl^-] = K.$$

The increase in value of $[Cl^-]$ due to addition of HCl without dilution causes an increase in the product. But K is always constant, therefore $[Na^+]$ must decrease to keep this value of K the same. But an increase of $[Cl^-]$ and decrease of $[Na^+]$ means the formation of NaCl molecules. Since the solution is already saturated a precipitate forms.

With a very low concentration of Cu^{++} ions in a solution there need be added only a small concentration of S^{--} ions to exceed the extremely small solubility product of copper sulfide:

$$[Cu^{++}] \times [S^{--}] = k.$$

The converse of the above must be that whenever the product of the concentrations of any two ions in a saturated solution is made less than the actual solubility product of this compound, any undissolved substance present must dissolve. If to a suspension of $Fe(OH)_3$ any acid is added, the precipitate dissolves:

$$\underset{\text{Undissolved}}{Fe(OH)_3} \rightleftarrows \underset{\text{Dissolved}}{Fe(OH)_3} \rightleftarrows Fe^{+++} + OH^- + OH^- + OH^-.$$

The H^+ ions of the acid unite with OH^- ions to form water. Consequently the product of the concentrations of the Fe^{+++} ions and OH^- ions falls below the solubility product and more precipitate must dissolve.

The Debye-Hückel Theory of Complete Ionization.—The effect of addition of a common ion to solutions of weak electrolytes such as acetic acid and ammonia is in good accord with the Law of Mass Action (page 211). But this law breaks down completely when applied to the addition of any neutral salt to dilute solutions of strong electrolytes. When an excess of NaCl or KCl is added to a 0.01 N HCl solution the solution becomes more actively acidic than before. By the Law of Mass Action there should be some repression of ionization of HCl due to the increase in the concentration from the added Cl^+ ion, yet the opposite is true. This strange phenomenon is called the "neutral salt effect."

By the fraction ionized is meant the ratio of H^+ ion concentration, for example, to the H^+ ion concentration possible if all the acid molecules were ionized. The activity coefficient is analogous, but is based on the modern Debye-Hückel theory that in dilute solutions of strong electrolytes practically all the molecules are ionized although a fraction are restricted in their freedom of movement by the restraining influence of oppositely charged neighbors.

Kendall suggests that the phrase "extent of ionization" should be interpreted as "apparent extent of ionization." Perhaps the fraction ionized does not change with change in concentration but rather, the ionic mobility.

Equilibrium in Acidic and Basic Solutions.—As shown by the facts of hydrolysis there is an equilibrium in pure water:

$$H^+ + OH^- \rightleftarrows H_2O.$$

Addition of an acid disturbs this equilibrium to the right and decreases the concentration of OH^- ions, perhaps almost to the vanishing point. Addition of a base to water also disturbs the equilibrium to the right but decreases the concentration of H^+ ions. In each case it is a matter of addition of a common ion, either H^+ ions or OH^- ions. "Mass action" expresses it. It is usual for us to think of an acid solution as marked by the presence of H^+ ions and entire absence of OH^- ions. Such is not the case. An acidic solution is merely one in which there are *more* H^+ ions than OH^- ions. A basic solution contains more OH^- ions than H^+ ions. A neutral solution contains H^+ and OH^- in the same concentration as in water.

Some indicators change color when the excess of H^+ ions reaches a definite concentration. For example, methyl orange does not change from yellow to pink until there are present a million times as many H^+ ions as OH^- ions.

EXERCISES

5. What is the effect of adding ammonium chloride to a solution of ammonium hydroxide?

6. A M/10 solution of acetic acid is ionized to the extent of 0.013. Calculate the ionization constant of acetic acid.

7. Are there any OH^- ions in a solution of an acid?

8. What is the Principle of Le Chatelier? Give an application.

9. What is Van't Hoff's law? Give an application.

10. Why are all ionizations reversible? How can you disturb the equilibrium?

11. Copper sulfate is very soluble and copper sulfide very insoluble. Which has the larger solubility product?

12. What is the Debye-Hückel theory of complete ionization?

13. Calculate the solubility product of the following:

silver acetate,	ionization	72	per	cent,	molar	solubility	0.059
lead chromate,	"	100	"	"	"	"	0.0000004
lead sulfate,	"	92	"	"	"	"	0.00013
barium sulfate,	"	98	"	"	"	"	0.00001
calcium sulfate,	"	52	"	"	"	"	0.015

14. In a molar solution of ammonium hydroxide the fraction ionized is .0047. Calculate the ionization constant.

15. What would happen to the acidity of a solution of hydrochoric acid if much sodium acetate were added? If any sodium salt of a weak acid were added?

Ionization increases with dilution -

CHAPTER XXIV

NITROGEN AND AMMONIA

NITROGEN

History of Nitrogen.—Because of its comparative inertness, nitrogen was one of the least interesting of elements in the free state until a generation ago. Now it is eagerly sought after by basic industries of war and peace. Rutherford, the Edinburgh botanist, discovered the element in 1772, but it was not really considered an element until Lavoisier studied it. He tried to name it "*azote*," but only the French accepted this name. The rest of the world called it nitrogen as soon as it was learned that it was an essential constituent of niter (KNO_3).

Occurrence.—Nitrogen is "as free as air," since it makes up four-fifths of the atmosphere. The nitrogen resting on every square foot of ground weighs almost a ton, while that resting on a square mile weighs 20,000,000 tons, enough, if converted into all the combined forms desired, to meet the world's needs for 12 years.

A small amount is found in the air as ammonia and oxides of nitrogen, but this is washed into the soil by rains.

Deposits of potassium nitrate (KNO_3) or "saltpeter" are found, but are not of much consequence although in 1928 a large deposit was discovered in central Australia. Sodium nitrate ($NaNO_3$), or Chili saltpeter, is one of the most important sources of nitrogen. In the rainless district of northern Chili there is a strip two miles wide by two hundred long and five feet thick that is rich in sodium nitrate. A little of the potassium salt occurs there also. By mixing solutions of sodium nitrate and potassium chloride, and manipulating the concentration and temperature, a supply of potassium nitrate more than adequate for the world's gunpowder needs is secured:

$$NaNO_3 + KCl \rightleftarrows NaCl + KNO_3.$$

This enormous deposit of sodium nitrate is also used extensively in the manufacture of nitric acid and fertilizers, so it has great economic significance. Since the discovery of the deposit in 1809, over 53,000,000 tons have been mined.

Since plants and animals eventually decay, their nitrogenous material is all-important in enriching the soil.

Preparation.[1]—It is a simple matter to pass dry air over hot copper, which removes the oxygen, forming copper oxide. Commercially this oxide is then reduced back to the metal by a stream of hot hydrogen or, better, natural gas and is ready for use again. The remaining nitrogen is not quite pure, since it contains argon, carbon dioxide, etc.

If phosphorus is burned ~~under a cylinder,~~ the oxide of phosphorus dissolves in the water, leaving the cylinder filled with nitrogen.

Exercise 1.—Why not secure nitrogen by passing ordinary moist air over red-hot iron?

The leading commercial source of nitrogen is now liquid air. On allowing this modern product to evaporate, the more volatile nitrogen escapes first and is used in the manufacture of ammonia. It is fortunate for the cost of the process that there is a large demand for the oxygen as well.

Ammonium nitrite is an excellent laboratory source of pure nitrogen, although too expensive for commercial use. This salt is unstable, so it must be prepared when needed. Solutions of ammonium chloride and sodium nitrite are mixed and heated gently:

$$NH_4Cl + NaNO_2 \rightleftarrows NaCl + NH_4NO_2$$
$$NH_4NO_2 \rightleftarrows 2\ H_2O + N_2.$$

Since all four substances are soluble, this is a reversible reaction, but the equilibrium is disturbed to the right on heating since gentle heating decomposes the ammonium nitrite.

Another laboratory reaction of interest occurs when ammonia is passed over hot copper oxide:

$$2\ NH_3 + 3\ CuO \longrightarrow N_2 + 3\ H_2O + 3\ Cu.$$

By weighing the copper oxide, the copper, and the water and collecting the nitrogen over an acid (to absorb excess ammonia), this experiment can serve as a splendid illustration of Gay-Lussac's law and as a means of determining certain equivalent weights.

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[1] An active form of nitrogen which is probably triatomic, N_3 (like ozone, O_3), has also been prepared.

Exercise 2.—If 238.71 g. of copper oxide were reduced by hot ammonia gas, how many liters of nitrogen would be obtained? How many liters of ammonia would be required?

Physical Properties.—Nitrogen is a colorless, odorless, tasteless gas, only slightly soluble in water. One liter weighs 1.2507 g., therefore it is a little lighter than air. At its critical temperature, −146°, it is liquefied by the critical pressure of 33 atmospheres. The liquid boils at −195.7° and freezes at −210.5°.

Exercise 3.—What two influences prevent all of the heavier oxygen of the air settling to the surface of the earth, while the lighter nitrogen rises to great heights? There really is a certain amount of gravity separation.

"Ice" of frozen nitrogen glows with a brilliant greenish-yellow light under bombardment by cathode rays.

Under the influence of the silent electric discharge molecular nitrogen yields some atomic nitrogen which is very unstable soon reverting to the ordinary form of N_2. In the atomic form nitrogen seems to be extremely active chemically. It even unites, to some extent, with the common diatomic nitrogen to form the unstable N_3, analogous to ozone.

Chemical Properties.—Nitrogen is found free in the atmosphere because it is so inactive. However it combines with oxygen at very high temperatures and with several elements when strongly heated. With magnesium, aluminum, calcium, silicon, titanium, lithium, boron, and some other elements it forms nitrides of some interest as possible sources of ammonia:

$$3\,Mg + N_2 \longrightarrow Mg_3N_2.$$

Hot calcium carbide unites with nitrogen to form calcium cyanamide. Bacteria on the roots of legumes such as clover, alfalfa, peas, and beans are able to tie up the atmospheric nitrogen in a combined form available for plant growth. The union of nitrogen with hydrogen under the stimulus of a catalyst will be discussed in the ammonia section.

Exercise 4.—The G. M. V. of nitrogen weighs 28 g. What is the formula of the gas?

The composition of ammonia can be redetermined in the laboratory very easily by passing the gas (dried by soda-lime) over heated copper oxide (wire form preferred), collecting the water formed in a weighed tube of soda-lime and collecting the free nitrogen over diluted acid.

$$2\,CuO + 2\,NH_3 \longrightarrow 2\,Cu + N_2 + 3\,H_2O.$$

The Cycle of Nitrogen in Nature.—Nitrogen is absolutely essential to plant life and hence to animal life (Fig. 94). Yet it may be feared that the available plant food in the soil will ultimately be used up. Nature has provided us to some extent with a nitrogen cycle. Atmospheric nitrogen is seized by bacteria growing on the roots of clover, alfalfa, and the other legumes and converted into protein compounds. Another class of bacteria convert these proteins into nitric acid. Apparently this powerful acid would play havoc with the crops. However, there is nearly always enough basic matter in the soil to neutralize the acid, forming nitrates. In a soil deficient in bases the nitrifying bacteria refuse to work—they themselves do not enjoy an acid environment—and the farmer is forced to lime the field. When the clover is plowed under, its protein becomes a rich asset in the soil, subject to further improvement, of course, by the nitrifying bacteria. Succeeding crops of grain utilize the nitrates, animals eat the grain, and ultimately atmospheric nitrogen has become lean meat (muscle). Truly a wonderful magic! When plants or animals decay, some nitrogen is returned to the air and the cycle begins again.

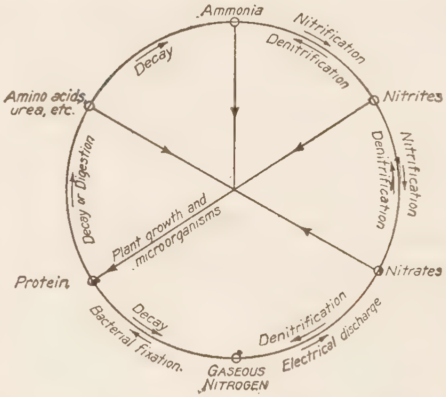
Ammonia
Nitrification
Denitrification
Nitrites
Nitrification
Denitrification
Nitrates
Denitrification
Electrical discharge
Gaseous Nitrogen
Bacterial fixation
Decay
Protein
Plant growth and microorganisms
Decay or Digestion
Amino acids, urea, etc.
Decay

Fig. 94.—The cycle of nitrogen in nature.

Uses of Nitrogen.—We have seen that nitrogen is vital to plant and animal growth. It is now forced to react with hydrogen to form ammonia and driven to react with oxygen to form nitric oxide and thus nitric acid. When added to hot calcium carbide a good fertilizer, cyanamide, is produced. Without nitric acid and ammonia we should have practically no explosives and be greatly limited in our stock of useful dyes and drugs. An atmosphere of pure oxygen undiluted with the inert nitrogen would accelerate combustion to a dangerous degree and be too active for animal respiration.

"Active" hydrogen reduces nitrites and nitrates to ammonia. If the hydrogen is prepared by zinc and a base the ammonia escapes, but if prepared by zinc and an acid the ammonia neutralizes the excess acid, forming a salt.

Most protein material, when boiled with concentrated sulfuric acid, is decomposed with formation of ammonia, or rather ammonium sulfate. This is the foundation of a famous method of food analysis.

Cyanides, when hydrolyzed with boiling alkaline solutions yield ammonia.

Preparation from Coal.—Soft coal contains one per cent, or a little more, of nitrogen. About one fifth of this is recovered on distillation as ammonia. The mixed gas of distillation is passed through wash water which retains the ammonia and some impurities. Later, lime is added to this ammonia liquor and steam is passed through. The ammonia is thus driven off and may be neutralized with sulfuric acid to form ammonium sulfate (about 20 pounds from one ton of coal). The rest of the nitrogen remains in the coke. In 1929 the United States produced 900,000 tons of ammonium sulfate from coal (estimated as about 190,000 tons of "fixed nitrogen").

Until recent years coke was made in beehive coke ovens, allowing the ammonia and other gases to waste on the air. Now in 1929 fully 90 per cent of all American coke is made in by-product ovens with recovery of the ammonia, benzene, tars, coal gas, etc.

AMMONIA

Ammonia has steadily risen in our esteem. Once of interest mainly as the pungent feature of a liniment, it later became important in the preparation of fertilizers, and during the World War rose to the rank of a military necessity. The fate of great nations hung upon their ability to produce more and more ammonia—from which they might make nitric acid for explosives. Now it dominates the future of agriculture.

Priestley (1774) was the first to prepare ammonia, collecting it over mercury. However, it was left to Berthollet to determine its true composition (1785). Faraday liquefied the gas in 1823.

Traces occur in the atmosphere, but there are no earth deposits of ammonia or its derivatives. On heating animal or plant substance containing combined nitrogen, ammonia is always formed. The name, "spirits of hartshorn," was given because it was once prepared by heating deer horns, hoofs, and such material. Bituminous coal contains combined nitrogen, and on distilling in absence of air great quantities of ammonia come off. Until recently this was almost the only source of this gas. It must not be imagined that there is any free ammonia locked up in the coal. Its elements merely unite during the heating.

Exercise 5.—What was the original source of the nitrogen in coal?

Preparation in the Laboratory.—The gas is conveniently prepared in the laboratory by warming a dry ammonium salt with lime or any other base. Since it is lighter than air, ammonia is collected by downward displacement of air (why not let it displace water?):

$$NH_4Cl + NaOH \longrightarrow NaCl + NH_4OH,$$
$$NH_4OH \longrightarrow H_2O + NH_3.$$

The ammonium hydroxide (NH_4OH) breaks down on heating into the gas and water. In fact warming a concentrated solution of ammonium hydroxide is often found a most convenient method of securing the gas.

For years Scotland has distilled her oil shales to get the oil. As a by-product enough ammonia is produced to form 42 pounds of ammonium sulfate per ton of shale. American oil shale deposits are enormous.

Nitrides react with water to form ammonia:

$$Mg_3N_2 + 6\,H_2O \longrightarrow 3\,Mg(OH)_2 + 2\,NH_3.$$

Physical Properties.—Ammonia is a colorless, pungent gas about one-half as heavy as air. One liter weighs 0.7708 g. Its critical temperature is 130° and critical pressure 115 atmospheres. At 10° it can be liquefied with only 6.5 atmospheres. Its extreme solubility in water is noteworthy as shown by the HCl or NH_3 fountain (Fig. 63, page 178). At 20° one volume of water absorbs 700 volumes of ammonia. The gas is also quite soluble in alcohol and in ether. Its heat of evaporation is higher than that of any other known liquid except water. The concentrated solution in water has a density of 0.9 and contains about 28 per cent of the gas.

The very great solubility of ammonia in water may be shown by the experiment represented in Fig. 63. The flask is filled with dry ammonia and a few drops of water are then forced into the flask by air pressure (breath). The ammonia dissolves in these few drops, thus greatly decreasing the pressure of gas in the flask. Consequently water from the bottle is forced up the tube like a fountain. Could you do this with hydrogen chloride?

Chemical Properties.—Long-continued breathing of air containing as little as one per cent ammonia produces serious results. The gas may be burned in air by the use of a device shown in Fig. 95. The air intake in the Fletcher burner must be closed (a sheet of tin foil serves) and the asbestos sheet heated first by an ordinary gas flame. Then by the use of **Y** tubes a stream of ammonia can be mixed with the other gas and finally all of the common gas shut off. This leaves ammonia alone burning with a yellow flame. In the presence of catalysts such as platinum it reacts with oxygen to form oxides of nitrogen and water, hence nitric acid.

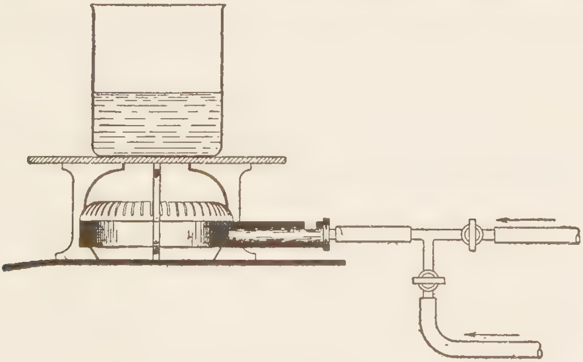

FIG. 95.—Burning ammonia in air.

Ammonia will even steal oxygen from metallic oxides. Its ability to reduce hot copper oxide has been mentioned:

$$3\,CuO + 2\,NH_3 \longrightarrow 3\,Cu + 3\,H_2O + N_2.$$

With sodium and potassium, ammonia reacts, when heated, to form amides. Sodamide is formed in this way:

$$2\,Na + 2\,NH_3 \longrightarrow 2\,NaNH_2 + H_2.$$

Acids react with the gas to form ammonium salts, but only in the presence of at least a trace of water:

$$NH_3 + HCl \longrightarrow NH_4Cl.$$

One of the most important reactions of ammonia is with water to form ammonium hydroxide:

$$NH_3 + H_2O \rightleftharpoons NH_4OH.$$

Ammonia reacts with some salts. With calcium chloride it forms $CaCl_2 \cdot 8\,NH_3$, hence the gas must be dried over solid sodium hydroxide or some other dry base.

Exercise 6.—Why not dry ammonia by bubbling through concentrated sulfuric acid?

Exercise 7.—When a definite volume of ammonia is subjected to prolonged electric sparking, what happens? What volume relations hold?

Ammonium amalgam is a remarkable substance formed by adding sodium amalgam (HgNa) to a cold, concentrated solution of ammonium chloride:

$$HgNa + NH_4Cl \longrightarrow NaCl + NH_4Hg.$$

The ammonium amalgam is greasy and spongy, rapidly decomposing into mercury, ammonia, and hydrogen. If the amalgam is considered an alloy, it seems that we have come close to isolating the hypothetical metal ammonium.

Uses.—Ammonia is the raw material for the Ostwald process of making nitric acid. It is combined with acids to make ammonium salts used in enormous quantities for fertilizers. Its salts are used in soldering, galvanizing, in dry batteries, and the gas itself is the chief refrigerant in commercial use.

In the modern ice plant ammonia under pressure is allowed to expand through a coil of metal pipe (Fig. 96). The expansion of the gas reduces the temperature of a brine surrounding the coils below the freezing point of pure water. A concentrated solution of calcium chloride is the usual brine, because it freezes several degrees lower than pure water. Cans of water are immersed in the brine and their contents frozen to ice. It is a simple matter to lift out the cams and empty them. In cold storage houses the rooms are chilled by pipes containing the circulating brine, and no ice need be made. Household refrigerators operated by electric power are now based on this principle. Power is needed to compress the expanded ammonia ready for use again. On compression much heat is developed, and this is removed by cooling the pipes with running water.

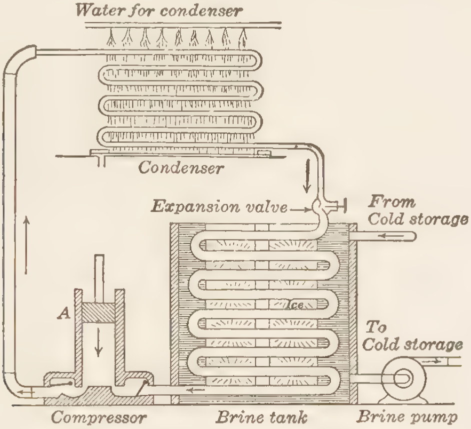

Fig. 96.—Diagram to show the principle of a refrigeration plant.

There are now more than 500,000 household electric refrigerators in the United States, using 35,000,000 pounds of anhydrous ammonia.

Exercise 8.—The heat of fusion of water is 79 calories, while the heat of evaporation of ammonia is 258 calories. How many grams of liquid ammonia must be allowed to expand to a gas in order to freeze 4 K. of ice?

Occasionally a pressure pipe bursts in a refrigerating plant and the air is filled with ammonia. Plumbers attempting to repair the breaks must wear gas masks. Sulfuric acid in the mask has been used as an absorbent, but copper sulfate is better. It unites with ammonia to form $CuSO_4 \cdot 4\ NH_3$ and has none of the unpleasant features of the acid.

Ammonium Hydroxide.—Ammonia not only dissolves freely in water, but to some extent reacts with water. The equilibrium conditions are given:

$$NH_3 + H_2O \rightleftarrows NH_4OH \rightleftarrows NH_4^+ + OH^-.$$

Ammonium hydroxide is listed as a very weak base. Although two-thirds of the ammonia present in a solution is there as dissolved molecular NH_3, according to T. S. Moore it is still true that the rest of it (NH_4OH) is only weakly ionized. The H^+ ions from any added acid removes the OH^- ions from the field and disturbs both equilibria to the right until all dissolved ammonia has passed through the ionic stage. Ionic reactions take place in liquefied ammonia.

Ammonium Salts.—Ammonium sulfate, formed by addition of ammonia water to sulfuric acid, is the salt usually used as a fertilizer.

Germany has great deposits of gypsum ($CaSO_4 \cdot 2\,H_2O$) but no sulfur or mineral sulfides from which to make sulfuric acid. To develop some degree of economic independence in this respect Germany has utilized the double decomposition between gypsum and ammonium carbonate in converting her synthetic ammonia into ammonium sulfate. In practice the pulverized calcium sulfate is treated with carbon dioxide and ammonia. The precipitated calcium carbonate is filtered off.

$$(NH_4)_2CO_3 + CaSO_4 \rightarrow (NH_4)_2SO_4 + CaCO_3.$$

Ammonium chloride is useful in soldering and galvanizing. It dissociates on heating into ammonia and hydrogen chloride, which reunite on cooling with appearance of a smoke—solid particles of ammonium chloride. If heated at one end of a long tube, the lighter ammonia, diffusing faster (see Graham's law), turns moist red litmus paper blue if the paper is placed at the other end.

Ammonium nitrate was used in enormous quantities during the World War as an explosive or in explosive mixtures. It is difficult to detonate, but once started it is effective. The supply of T. N. T. was never adequate, but fortunately it was found that this expensive explosive could be mixed with four times its weight of the cheaper and plentiful ammonium nitrate without loss of power.

Ammonium bicarbonate (NH_4HCO_3) is used as a partial substitute for yeast in baking crackers.

All ammonium salts decompose on heating, but they do not all release ammonia. However, any ammonium salt heated with a base releases ammonia, which can be recognized by smell or its effect on wet red litmus paper. It is the only common volatile base:

$$(1)\quad NH_4Cl + NaOH \longrightarrow NaCl + NH_4OH,$$
$$(2)\quad NH_4OH \longrightarrow NH_3 + H_2O.$$

Complex Ammonia Compounds.—Insoluble silver compounds dissolve in "ammonia water." Silver chloride may be used as an illustration:

$$AgCl + 2\,NH_3 \longrightarrow Ag(NH_3)_2Cl.$$

On ionization the ammonia goes with the silver and in electrolysis is released at the cathode. Addition of ammonium hydroxide to a copper salt solution first precipitates copper hydroxide or, rather, a basic copper salt. Excess dissolves this, yielding a beautiful azure-blue solution. With copper sulfate the product is $Cu(NH_3)_4SO_4$ and with copper chloride $Cu(NH_3)_4Cl_2$. All these complex salts yield the $Cu(NH_3)_4^{++}$ ion. The formation of the peculiar blue color, quite different from the blue of Cu^{++} ion, is a test for copper compounds.

Other Compounds of Nitrogen.—Hydrazine, N_2H_4, is a poisonous liquid boiling at 113.5°. It is a strong reducing agent, forms hydrates with water and salts with acids.

Hydrazoic acid, HN_3, a colorless liquid boiling at 37°, forms a number of explosive salts called azides. The acid itself is very unstable.

Hydroxylamine, NH_2OH, a white solid melting at 33°, forms with acids such salts as hydroxylamine hydrochlorid, NH_4OCl or $NH_2OH \cdot HCl$.

Nitrogen trichloride, NCl_3, is an extremely explosive oily liquid, and nitrogen iodide, $NI_3 \cdot NH_3$, is a dangerously explosive solid.

EXERCISES

9. What weight of ammonium chloride must be used in the preparation of the ammonia necessary for 2 liters of 0.2 N ammonium hydroxide?

10. If 15 g. of magnesium nitride are treated with hot water what weight of ammonia will be obtained? If this ammonia is made up to 500 cc. what will be the normality? How many cc. of 0.15 normal hydrochloric acid will it take to neutralize 25 cc.?

11. What is the percentage by weight of nitrogen in the following: NH_3, KNO_3, KNO_2, N_2O_5, and Mg_3N_2?

12. How many liters of nitrogen can be obtained by treating 250 cc. of a 20 per cent solution of sodium nitrite (Sp. gr. 1.2) with ammonium chloride?

13. If you were denied the use of a liquid air apparatus but were permitted to burn hydrogen (supply guaranteed) in air, could you prepare a mixture of approximately three volumes of free hydrogen and one volume of free nitrogen for conversion to ammonia by a Haber catalytic bomb? Disregard the argon in air.

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CHAPTER XXV

NITROGEN FIXATION

The real "conquest of the air" was not made by the inventors of airplanes and dirigible airships, but by the chemist. Before the end of the last century a world wheat famine was predicted by eminent scientists because of the probable early exhaustion of the sodium nitrate beds of Chili. The population of the world doubled between 1800 and 1900 and the rate of increase is still alarming. The chemist has driven off, for a long time to come, the specter of world starvation with its accompanying chaos, warfare, and human misery. His conquest of the air was the ***fixation of atmospheric nitrogen into compounds available as plant food or otherwise useful to mankind.*** Not by a single method did he succeed, but by three or four triumphs.

A nation lacking an adequate supply of combined nitrogen can be great neither in peace nor in war. Nitrogen compounds are essential to agriculture, to many basic industries, and are absolutely essential to the manufacture of all useful explosives.

Fixation of Nitrogen by the Arc Process.—The most spectacular of all fixation processes, though not the most economical, called upon the lightning for a model. It has long been known that the great heat of the lightning flash caused a little oxygen and nitrogen of the air to combine, forming oxides of nitrogen.

Nature has been outdone in the laboratory. By one process a stream of electric sparks in a long tube produced a commercial quantity of nitric oxide but the most successful process of this type (the Birkeland-Eyde) utilizes the great heat of the electric arc. Air is blown through an arc distorted to a six-foot disk by a magnetic field. One per cent or more of the air, at a temperature of 3000° to 3500°, is converted into nitric oxide, which is cooled to permit formation of nitrogen dioxide (NO_2) by union with the excess oxygen. When this secondary product is passed through absorbing towers, down which water splashes, the final reaction yields nitric acid.

imbalance Chap.
Reaction more rapid at high T.

$$(1)\quad N_2 + O_2 \longrightarrow 2\,NO, \text{ colorless nitric oxide.}$$

$$(2)\quad 2\,NO + O_2 \longrightarrow 2\,NO_2, \text{ red-brown nitrogen dioxide (below } 620^\circ\text{).}$$

$$(3)\quad H_2O + 3\,NO_2 \longrightarrow 2\,HNO_3 + NO.$$

Most of the product is made to react with limestone to yield calcium nitrate, a very good fertilizer:

$$CaCO_3 + 2\,HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O + CO_2.$$

It is only in Norway that electric power is cheap enough to maintain the arc process in competition with other processes requiring far less electric energy. Even there the arc process is being displaced by the direct synthesis of ammonia.

The Cyanamide Process.—In 1895 the German chemists, Caro and Frank, ***coupled nitrogen from the air to calcium carbide, forming calcium cyanamide ($CaCN_2$),*** a useful fertilizer and a source of ammonia. It was not until 1906, however, that commercial plants were built (in Germany and Italy). Calcium carbide was made by heating coke with lime in the electric furnace. Up to that time it had been used only as a source of acetylene. Caro and Frank gave the world a valuable reaction when they passed nitrogen (not air) over this carbide at about 1100° C. The product, cyanamide, was next treated with steam under pressure to yield ammonia.

$$\begin{aligned} CaCO_3 &\longrightarrow CaO + CO_2,\\ 3\,C + CaO &\longrightarrow CaC_2 + CO,\\ CaC_2 + N_2 &\longrightarrow CaCN_2 + C,\\ CaCN_2 + H_2O &\longrightarrow CaCO_3 + 2\,NH_3. \end{aligned}$$

Cyanamide itself, if first moistened to decompose any residual carbide and oiled to hold down dust, may be used directly as a fertilizer, but such use is not as satisfactory as the conversion into ammonia and ammonium salts for plant food. The cyanamide industry is losing ground relatively.

The great Muscle Shoals cyanamide plant (No. 2), built by the nation as a war measure, is equipped to convert the cyanamide nitrogen into ammonia and so into ammonium sulfate or into nitric acid. Although not operated since the war it is a potential source of fertilizer to the extent of 200,000 tons of ammonium sulfate annually. It is also possible to convert cyanamide into use as an excellent fertilizer containing over 40 per cent available nitrogen. Although the cyanamide process of nitrogen fixation has lost, probably forever, its leading place it has some advantages such as low power and low labor costs.

FERTILIZER PRODUCTS OF NITROGEN FIXATION PROCESSES

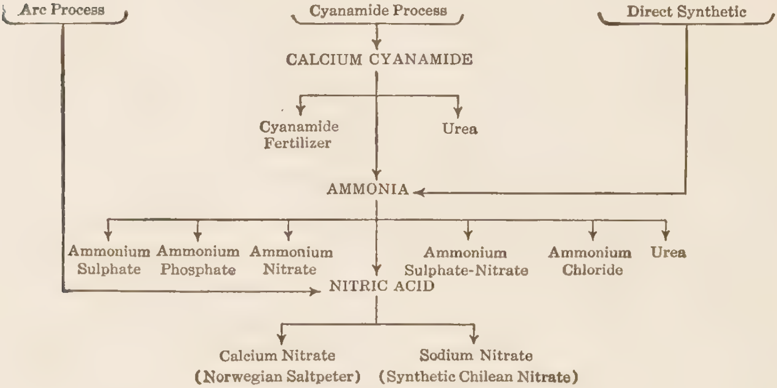

Arc Process
Cyanamide Process
Direct Synthetic
CALCIUM CYANAMIDE
Cyanamide Fertilizer
Urea
AMMONIA
Ammonium Sulphate
Ammonium Phosphate
Ammonium Nitrate
Ammonium Sulphate-Nitrate
Ammonium Chloride
Urea
NITRIC ACID
Calcium Nitrate (Norwegian Saltpeter)
Sodium Nitrate (Synthetic Chilean Nitrate)

FIG. 97.

THE DIRECT SYNTHESIS OF AMMONIA

The Haber Process.—The process of making ammonia by direct union of the elements was first made a commercial success by Haber in Germany (1913). This was, perhaps, the greatest triumph of chemical engineering, and Germany may well be proud of Haber. Without his process, she could not have continued the Great War a year for lack of high explosives. Ammonia ⟶ nitric acid ⟶ explosives, was the order of the day. Her other sources of ammonia, though great, were inadequate. Without control of the sea, the usual importation of sodium nitrate from Chili was impossible. So a scarcity of nitric acid would have been inevitable but for the brilliant Haber.

Haber developed the reaction between nitrogen and hydrogen:

$$N_2 + 3\,H_2 \rightleftarrows 2\,NH_3.$$

Catalyst used to fasten reaction

Pure

At ordinary temperatures their union to form ammonia is so slow as to be imperceptible, while at high temperatures the ammonia is decomposed rapidly. In fact above 700° it is almost completely decomposed. Obviously a moderate temperature is desirable, but even so, the yield is poor. Haber discovered that at 200 atmospheres pressure and 500° temperature the formation of ammonia proceeds satisfactorily if osmium or uranium is present as a catalyst. Working at such high temperatures and pressures is difficult, yet success was obtained. Chrome steel, free from carbon, must be used for the apparatus, as otherwise the hydrogen would remove the carbon from ordinary steel, leaving "rotten steel." The catalyst now used is essentially iron with some substances such as the oxides of aluminum and potassium to promote the catalytic action. Only about 8 per cent of the nitrogen is converted into ammonia (maximum yield) even when the unreacted gases are circulated again through the catalyst.

It is remarkable that iron and molybdenum are poor catalysts singly for the Haber reaction but intimately mixed form one of the best catalysts. Iron forms an unstable hydride and molybdenum an unstable nitride. Does this action bring the nitrogen and hydrogen together?

The Casale Process.—The Casale process, developed in Italy and now widely used, operates under a pressure of 500 atmospheres and at about 600° C. A maximum conversion of 40 per cent of the nitrogen with recirculation is claimed. It is only a special modification of the original Haber process.

The Claude Process.—Applying the principle of Le Chatelier to the limit, Claude, in France, developed a highly successful improvement on Haber's process by operating at 1000 atmospheres pressure. The maximum conversion claimed is 40 per cent of the nitrogen, although the gases are not recirculated.

The Fauser Process developed in Italy closely resembles the Haber method. Operating at 250 atmospheres and 550° C. to 600° C., it differs mainly in mechanical features.

The American Processes.—Modifications of Haber's process developed in America operate at 100–300 atmospheres pressure and at 500° C., with an improved catalytic mixture. However, the Claude, the Casale and the Haber-Bosch processes are all operated in the United States under lease.

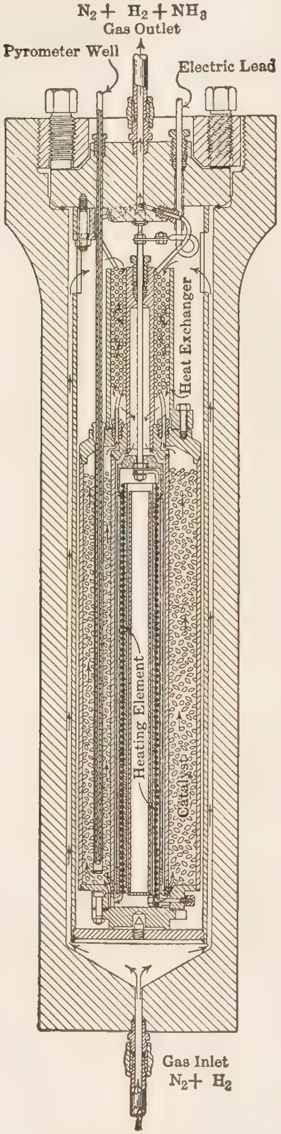


FIG. 98.—Cross section of the ammonia converter, or bomb, for the manufacture of ammonia from hydrogen and nitrogen.

Sources of Hydrogen for Direct Ammonia Synthesis.—In France (Claude process) hydrogen is removed from coke oven gas by a liquefaction process but the market value of coal gas in America may be too high to make this a suitable source. In Italy (Casale process) cheap electricity leads to some use of pure electrolytic hydrogen from water. The oxygen is removed from air by a hydrogen flame and the pure water condensed used as the source of electrolytic hydrogen. The original German Haber process obtained its hydrogen from water gas (coke and steam) by methods outlined in the Hydrogen chapter (page 73), and this seems to suit American costs best at present.

Of course small ammonia plants can and do operate in connection with the electrolytic manufacture of sodium hydroxide and chlorine, where hydrogen is a by-product.

One company in the United States manufactures butyl alcohol, for the solvent industry, by the fermentation of corn. As a by-product of this particular type of fermentation enormous volumes of free hydrogen are obtained and this is now being converted directly into 15 tons of ammonia daily.

The necessity of removing from the nitrogen (liquid air source) and hydrogen all such catalyst poisons as carbon monoxide, sulfur compounds, phosphine, and water, adds to the cost.

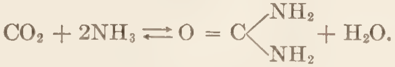
The World's Fixed Nitrogen Supply
(1929)

Direct synthetic ammonia	980,000	tons of fixed nitrogen	
Cyanamide	231,000	“ “ “ “	
Arc process nitrate	30,000	“ “ “ “	(or less)
Coke-oven ammonia	414,000	“ “ combined nitrogen	
Chili saltpeter	540,000	“ “ “ “	

The world's demand for inorganic fixed nitrogen is increasing at the rate of 100,000 tons (estimated as nitrogen) each year and there is no lower rate of increase in sight.

In the United States the increase in direct synthetic ammonia production is so rapid that 1930 will probably see over 100,000 tons of nitrogen so converted into ammonia. By-product coke ovens will also reach a capacity of 200,000 tons of ammonia for 1930, making a total fully twice our war needs. Germany alone fixes 900,000 tons of nitrogen in various ways. Agriculture will continue to profit greatly by this remarkable development.

Urea, a white crystalline solid, is now made as a fertilizer by reaction between ammonia and carbon dioxide under exact conditions of temperature and pressure.



$$CO_2 + 2NH_3 \rightleftharpoons O = C\begin{matrix} \diagup NH_2 \\ \diagdown NH_2 \end{matrix} + H_2O.$$

Soil Fertility

Fixation of Nitrogen by Bacteria.—Bacteria, those microscopic plants of the fungus type which cause so many of our diseases, are wonderful little chemists. In the human body they make poisons that sometimes kill. In the soil some types "fix" the free nitrogen of the air into nitric acid, which, of course, reacts with the basic material always in the soil to form nitrates, choice plant food. The nitrifying types are not found in all soils, but they are always found in little lumps or nodules attached to the roots of clover, alfalfa, cowpeas, and other legumes. Clover thrives on a soil that contains enough of these friendly bacteria. Sometimes the farmer inoculates poor soil with soil from a good field to start bacterial growth. One gram of rich soil may contain millions of bacteria. As a good air supply is necessary to stimulate nitrate formation, soil must not be allowed to become too compact or water-logged. Organic matter (humus) is also needed to supply food for bacteria.

There are other types of bacteria in soil, the ammonifiers, for example, that tear down complex nitrogen compounds into ammonia, and a pernicious type that denitrifies, or reverses, to some extent, the work of the nitrifiers, especially when the air supply is deficient.

Problem Yet To Be Solved.—To learn how bacteria, without the high temperature of the arc process or the great pressure of the synthetic ammonia processes, are able to "fix" the free nitrogen of the air.

Plant Food.—It is generally believed that only ten chemical elements are necessary as food materials—nitrogen, phosphorus, potassium, carbon, hydrogen, oxygen, sulfur, calcium, iron, and magnesium—but recently it has been demonstrated that manganese, zinc, and boron in traces, at least, are essential to the healthy growth of certain plants. Ten of these elements are supplied in most soils (supplemented by the atmosphere), but heavy cropping finally forces a fertilizing replacement of nitrogen, potassium, and phosphorus compounds.

PLANT FOOD CONSTITUENTS TAKEN FROM THE GROUND BY CROPS GROWN ON ONE ACRE (VAN SLYKE)

KIND OF CROP	AMOUNT	NITROGEN	PHOSPHORIC ACID	POTASH
Corn	25 bu.	39.2 lbs.	13.8 lbs.	27.6 lbs.
Wheat	25 bu.	42.5 lbs.	16.6 lbs.	21.0 lbs.
Oats	25 bu.	24.0 lbs.	9.0 lbs.	20.4 lbs.
Beans	25 bu.	88.0 lbs.	24.0 lbs.	57.5 lbs.
Potatoes	150 bu.	31.5 lbs.	13.5 lbs.	45.0 lbs.
Beets	25,000 lbs.	62.5 lbs.	25.0 lbs.	125.0 lbs.
Cotton	300 lbs.	40.6 lbs.	14.3 lbs.	32.2 lbs.
Tobacco	1,000 lbs.	59.0 lbs.	7.7 lbs.	78.0 lbs.
Sugar cane	52,000 lbs.	41.4 lbs.	22.6 lbs.	36.3 lbs.
Buckwheat	20 bu.	77.5 lbs.	13.5 lbs.	60.5 lbs.

Decayed organic matter (from stable manures and plowed-under crops) called "humus" is essential for it retains water, binds sandy soils, and loosens clay soils, renders much insoluble plant food available, holds in combination large quantities of useful lime, and aids in the growth of beneficial bacteria. The physical and biological condition of soils is almost as important as the chemical composition.

The sources of potassium salts and phosphates are discussed in other sections of the text.

Yeast as a Supplement to Farm Crops.—Yeast is an insignificant plant not ordinarily classed as a farm crop, but it has mighty potentialities. When air nitrogen has first been fixed by the chemist as an ammonium salt the lowly yeast plant can transform this salt with sugar and other chemicals fed it into nutritious protein, comparing favorably with lean beef, except in flavor. Doubtless new and well-flavored varieties of yeast will be developed.

Dr. H. E. Barnard asserts that "30 men working in a factory the size of a city block can produce in the form of yeast as much food as 1,000 farmers tilling 57,000 acres under ordinary agricultural conditions. To the chemist the Malthusian doctrine is but the sad reflection of a pessimistic world."

EXERCISES

1. The common "2–8–2" mixed fertilizer contains the equivalent of 2 per cent ammonia (NH_3), 8 per cent of phosphoric anhydride (P_2O_5), and 2 per cent of potassium oxide, or "potash" (K_2O). Get the local prices of $(NH_4)_2SO_4$, $Ca\ (HPO_4)_2$ and KCl, and calculate the cost of one ton of a 2–8–2 fertilizer. What is the actual cost?
2. If overcrowding leads to war, how can the yeast plant work for peace?
3. What are the sources of hydrogen for Nitrogen Fixation?

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Electrical Discharge —

$N_2 + O_2 \rightarrow 2NO$.

$2NO + O_2 \rightarrow NO_2$

By H_2O converted N_2O_3 + N_2O_5 — or HNO_2, HNO

These are neutralized by bases to form salts as —

$Ca(NO_3)_2$, $NaNO_3$ (found in Chile) called Saltpe

CHAPTER XXVI

THE OXIDES OF NITROGEN

A Partial Comparison of the Oxides of Nitrogen

N_2O	Nitrous oxide	Colorless gas	Heating NH_4NO_3
NO	Nitric oxide	Colorless gas	Diluted HNO_3 on Cu
N_2O_3	Nitrogen trioxide	Blue liquid at − 21°	Cooling $NO + NO_2 \rightleftarrows N_2O_3$
NO_2	Nitrogen dioxide	Red-brown gas	Conc. HNO_3 on Cu
N_2O_4	Nitrogen tetroxide	Colorless gas	Cooling $2\ NO_2 \rightleftarrows N_2O_4$
N_2O_5	Nitrogen pentoxide	White solid	Dehydrating HNO_3 by P_2O_5

Nitrous Oxide.—It was Priestley who in 1772 first prepared nitrous oxide gas by reduction of nitric oxide with moist iron filings. Since it was thought to be poisonous, Sir Humphry Davy was a rash young man when he breathed some of it to learn its properties. The hysteria occasionally produced by nitrous oxide earned for it the name "laughing gas." The gas is now made by carefully heating ammonium nitrate. (At too high temperatures ammonium nitrate may explode with terrific violence.)

$$NH_4NO_3 \longrightarrow 2\ H_2O + N_2O.$$

Exercise 1.—What other ammonium salt is heated to prepare pure nitrogen?

Liquid nitrous oxide boils at −90°. Since it is an endothermic compound, it is unstable, liberating 18,000 cal. per gram molecule on decomposing. Consequently such substances as charcoal, sulfur, and phosphorus burn in an atmosphere of nitrous oxide almost as vigorously as in oxygen. Yet the human body is unable to utilize its oxygen content. That is why oxygen must be mixed with this gas when used as an anæsthetic. Formerly only dentists used this pleasant, quick-acting anæsthetic, but in recent years it has been widely used by surgeons.

Since nitrous oxide is rather soluble, it is usually collected over warm water. Unlike oxygen it does not unite with nitric oxide to form red-brown fumes of NO_2.

✓ **Nitric Oxide.**—Although Cavendish in 1766 made this gas by passing electric sparks through a mixture of oxygen and nitrogen, and the lightning flash in air has been doing it for ages, scientists had done almost nothing with this reaction before the present century. But suddenly it became of such great importance that war and agriculture seemed likely to depend upon it.

Nitric oxide is a colorless gas slightly soluble in water. The liquid boils at −153.6°. This gas is easily prepared by the action of somewhat diluted nitric acid on copper:

$$3\,Cu + 8\,HNO_3 \longrightarrow 3\,Cu(NO_3)_2 + 2\,NO + 4\,H_2O.$$

In making nitric oxide a red-brown gas is first observed and then after this product is swept out of the generating flask it is replaced by a colorless gas. The explanation is simple. Nitric oxide is colorless but reacts with oxygen of the air to form red-brown nitrogen dioxide:

$$2\,NO + O_2 \longrightarrow 2\,NO_2.$$

The first reaction in the catalytic oxidation of ammonia by air is

$$4\,NH_3 + 5\,O_2 \longrightarrow 4\,NO + 6\,H_2O.$$

✓ **Nitrogen Dioxide (Peroxide).**—This very poisonous gas is made by heating pulverized lead nitrate or, in fact, the nitrate of any heavy metal:

$$2\,Pb(NO_3)_2 \longrightarrow 2\,PbO + O_2 + 4\,NO_2.$$

Concentrated nitric acid reacts with copper to release this gas:

$$4\,HNO_3 + Cu \longrightarrow Cu(NO_3)_2 + 2\,H_2O + 2\,NO_2.$$

It will be noted here that dilute nitric acid on copper forms nitric oxide. The water of the dilute acid probably reacts with any nitrogen peroxide formed, producing nitric acid and nitric oxide. If it be argued that the first product, no matter what the concentration, is nitric oxide, then it can be said that concentrated nitric acid would oxidize this gas to nitrogen dioxide. Either explanation is good. In preparing nitric acid there is always some decomposition with brown nitrogen dioxide as one product.

A study of the density of this gas at different temperatures is interesting. Molecular weights calculated from the density are about 92 at 20°; 56 at 70°; and 46 at 154°. The formula NO_2 calls for a molecular weight of 46, but evidently at 20° the molecules must unite to form N_2O_4 with double this molecular weight. Consequently below 20° only colorless nitrogen tetroxide (N_2O_4) exists. This dissociates completely into nitrogen dioxide (NO_2) at 154°. At intermediate temperatures a mixture of the two exists with corresponding densities. Above 620° all the NO_2 dissociates:

$$\underset{\text{Colorless}}{N_2O_4} \rightleftharpoons \underset{\text{Brown}}{2\ NO_2} \rightleftharpoons \underset{\text{Colorless}}{2\ NO + O_2}.$$

Nitrogen dioxide supports combustion with difficulty. Its most interesting reaction is with water:

$$\text{Cold } H_2O + N_2O_4 \longrightarrow HNO_3 + HNO_2,$$
$$3\ HNO_2 \longrightarrow HNO_3 + H_2O + 2\ NO, \text{ faster on warming.}$$

The reason there is no nitrous acid (HNO_2) formed in hot water is that it is decomposed by heat.

Exercise 2.—Could NO_2 be made at 700°?

Exercise 3.—If a mixture of heated air and nitrogen dioxide were led through a tower down which a spray of water fell, what would become of the nitric oxide by-product?

Nitrogen Trioxide.—This substance is formed by cooling a mixture of nitric oxide and nitrogen dioxide to −21° and appears then as a blue liquid. It dissociates well below room temperature so as a gas it is really the brown mixture of $NO + NO_2$. The equilibrium changes with the temperature:

$$N_2O_3 \rightleftharpoons NO_2 + NO.$$

The same gas mixture is formed when arsenic trioxide (As_2O_3) is heated with concentrated nitric acid and when water is added to nitrosyl sulfuric acid. (See lead-chamber process.) The catalyst in this lead-chamber process is usually called nitrogen trioxide, but it is apparent now that at the temperature of the chambers only $NO + NO_2$ could exist.

Exercise 4.—What influence would an excess of air have on the equilibrium given above?

Nitrogen Pentoxide.—This white solid is prepared by removing the elements of water from pure anhydrous nitric acid with phosphorous pentoxide. It is mainly a scientific curiosity, as the anhydride of nitric acid:

$$2\ HNO_3 + P_2O_5 \longrightarrow 2\ HPO_3 + N_2O_5.$$

EXERCISES

5. Nitrous oxide, when heated to high temperature, decomposes into nitrogen and oxygen. If 8 liters of nitrous oxide are decomposed by heat, what will be the volume of the resulting gas?

6. How many grams of ammonium nitrate would be required for the preparation of 12 liters of nitrous oxide measured at 20° and 10 atmospheres?

7. Twelve cc. of a 0.7 normal solution of nitric acid are treated with excess ferrous sulfate and sulfuric acid. What volume of nitric oxide is obtained?

8. A student once answered the question "How could you make oxygen from the air?" by this equation:

$$2\,N_5O \rightarrow O_2 + N_{10}.$$

What is wrong? What led him to this answer?

CHAPTER XXVII

NITRIC AND NITROUS ACIDS AND THEIR SALTS

Nitrates in Nature.—The largest deposit of nitrates is the sodium nitrate bed in the rainless Atacama Desert of Northern Chili. Scattered over an area from 3 to 30 miles wide and 400 miles long are deposits of nitrate bearing earth called caliche. Since the first operation of this great fertilizer bed in 1825 over 57,000,000 tons of Chili saltpeter have been exported and the annual production is about 2,500,000 tons. In Russian Turkestan there is a great deposit yet unworked, but in time it will maintain the fertility of Siberian wheat fields.

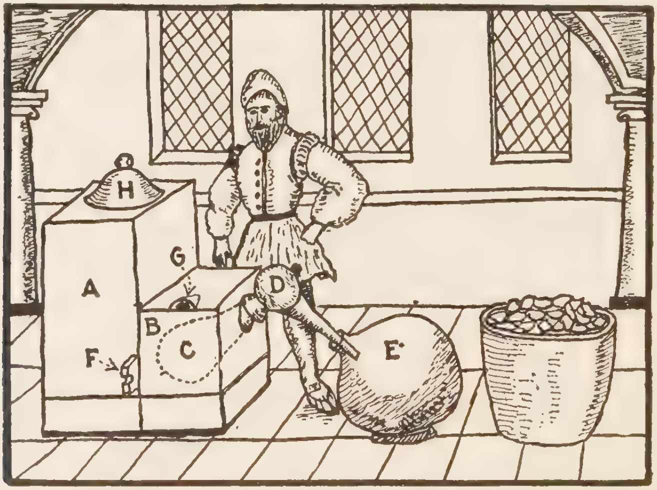


FIG. 99.—Lazarus Ercker's Apparatus for Aqua Fortis (Nitric Acid).

This is dated 1580 and the letters indicate the following: *A*—heating tower. *B*—Side oven. *C*—Flask. *D*—Helmet. *E*—Receiver. *F*—Damper. *G*—Gas outlet. *H*—Tower cover.

Potassium nitrate occurs to a limited extent in India (Bengal saltpeter) and is formed when organic matter decays in contact with wood ashes. A large deposit has recently been found in Central Australia.

Nitric Acid.—This acid has played a great rôle in history (since the ninth century) and is even now at the front of the stage. Its salts are important fertilizers, supplementing ammonium sulfate and the other soluble nitrogen compounds. Centuries ago one of its salts made gunpowder possible and now all of our modern high explosives which changed the map of Europe in short order are made by the use of this acid. The arts of peace, too, are finding some of its products of very great service. Over 90,000 tons of nitric acid are made yearly in the United States.

Preparation from Sodium Nitrate.—The first record of nitric acid manufacture was by Geber, a famous alchemist living from 750 to 800, A.D. He made it by heating together potassium nitrate, "copper vitriol" ($CuSO_4 \cdot 5\,H_2O$) and alum. Of course the sulfuric acid formed by heating dry, impure sulfates released nitric acid ("aqua fortis," as Geber named it) from the potassium nitrate. Basil Valentine in the fifteenth century simplified the process by heating a mixture of sodium nitrate and "oil of vitriol" (concentrated sulfuric acid). The more volatile nitric acid escaped into a condenser.

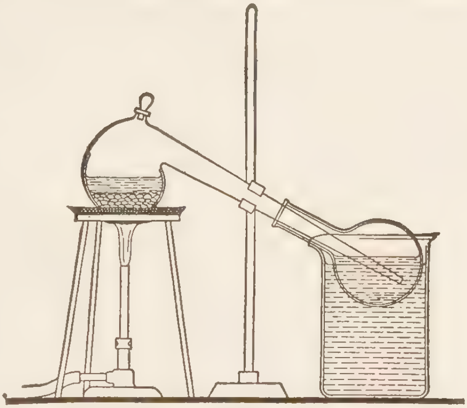


FIG. 100.—Laboratory preparation of nitric acid.

This ancient process still survives. In the laboratory a glass retort, with a cooled flask as condenser, is used (Figure 100). Two reactions may occur, depending upon the relative excess of sodium nitrate and the temperature.

$$(1)\quad NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3,$$
$$(2)\quad 2\,NaNO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HNO_3.$$

The first reaction is favored because it goes to practical completion below 200° C., while the second requires a temperature of 900° C. for completion. Furthermore, at such elevated temperatures nitric acid is decomposed and lost to a costly extent.

Cast-iron stills are used commercially and the vapors are condensed in glass tubes or, more recently, in fused quartz or duriron tubes. Duriron is an iron containing 16 per cent of silicon and is very hard and brittle. It resists corrosion by hot, concentrated nitric acid. An alloy steel containing 16 per cent Cr, 1 per cent Si, and less than 0.12 per cent carbon is making a place in the industry, even in transportion of the acid. There is some decomposition of the acid on distilling, so it is sometimes distilled under reduced pressure and consequently lower temperature:

$$4\ HNO_3 \longrightarrow 4\ NO_2 + O_2 + 2\ H_2O.$$

By redistilling with concentrated sulfuric acid the water of partial decomposition is removed and by bubbling air through the distillate the red nitrogen dioxide (NO_2) is removed. The anhydrous acid is rather unstable, however, so the ordinary "concentrated" acid of commerce is made by heating sodium nitrate with somewhat diluted sulfuric acid. thus securing a product which is 68 per cent nitric acid and 32 per cent water.

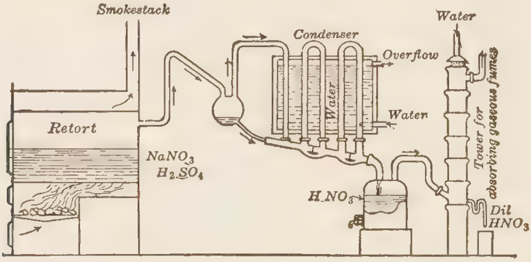


FIG. 101.—Commercial preparation of nitric acid.

The "niter cake" ($NaHSO_4$) is used somewhat in pickling the scale off iron or steel to be galvanized or tinned, but in general it is a drug on the market. It could be heated with sodium chloride to yield more hydrogen chloride.

The nitric acid vapors pass into the condensing system mixed with such decomposition products as oxides of nitrogen, oxygen, and water vapor. Since the temperature of the vapors as they are released varies from 110° C. to 130° C. a glance at the table following shows that 10 to 20 per cent of the nitric acid formed is thermally decomposed. As the products cool some recombination takes place.

DECOMPOSITION OF NITRIC ACID

CENTIGRADE TEMPERATURE	PER CENT DISSOCIATED
86	9.53
100	11.77
130	18.79
160	28.96
190	49.34
220	72.07
250	93.03
256	100.00

√ **The Arc Process.**—The Americans, Bradley and Lovejoy, at Niagara Falls, were the first (1902) to make nitric acid in quantity by the action of the electric arc on air, but it was left to the Norwegians, Birkeland and Eyde, to achieve commercial success (1903–1905). By their spectacular process air is blown through an electric arc distorted to a disk six feet in diameter, by a magnetic field. This gives better contact. The nitric oxide formed unites directly with excess oxygen and this secondary product, nitrogen dioxide, is brought in contact with water to form nitric acid. The nitric oxide evolved as in equation (3) reacts with more oxygen as in (2) and is not lost.

$$\begin{aligned} &(1) \qquad N_2 + O_2 \longrightarrow 2\,NO, \\ &(2) \qquad 2\,NO + O_2 \longrightarrow 2\,NO_2, \\ &(3) \quad \text{Hot } H_2O + 3\,NO_2 \longrightarrow 2\,HNO_3 + NO. \end{aligned}$$

The temperature of the arc is 3000°–3500°. Yet the second reaction will not take place at all above 620°. Nitrogen dioxide is completely decomposed at that temperature. Therefore the hot gases are cooled as rapidly as possible in chrome steel tubes to about 50° and led through a spray of water in a chrome steel tower. The nitric acid formed is only of 50 per cent concentration and requires concentrating by distillation. Any oxides escaping from this tower are led through a second or third splash tower. These are filled with rough lumps of limestone. The very dilute acid formed reacts with the limestone to produce calcium nitrate (equation ?), a good fertilizer. $CaO + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O$

It was once thought that this method of utilizing air nitrogen was the only hope of permanent agriculture, but the Haber and cyanamide processes have since surpassed the Birkeland-Eyde in effectiveness.

The Ostwald Ammonia Oxidation Process.—The essential supplement to Haber's method of making ammonia from its elements was Ostwald's oxidation of ammonia to nitric acid. The following equations give the steps.

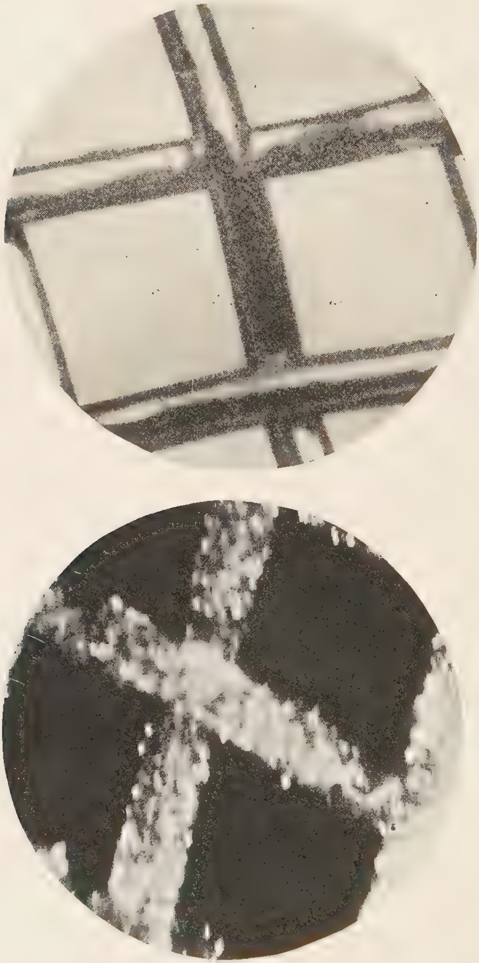


FIG. 102.—Platinum gauze (magnified) before and after its use as in the catalytic oxidation of ammonia.

$$4\ NH_3 + 5\ O_2 \longrightarrow 4\ NO + 6\ H_2O + 214{,}200\ \text{Cal.},$$
$$2\ NO + O_2 \longrightarrow 2\ NO_2,$$
$$3\ NO_2 + H_2O \longrightarrow 2\ HNO_3 + NO.$$

Ammonia mixed with ten times its volume of air is passed through a gauze of platinum wire at 600° and above, which catalyzes the reaction. Contact of less than 0.01 second is sufficient. The reaction is exothermicand the right temperature is maintained by regulating the flow of the gases. As with the Birkeland-Eyde process the fundamental idea had been known for generations, but it took an Ostwald to apply it successfully. During the World War Germany depended on this oxidation of ammonia, and the United States spent huge sums on a plant in Alabama in an attempt to develop both the Haber and Ostwald processes for military needs. It is possible that this plant will be operated in peace times for agricultural needs.

The platinum gauze, 80–150 mesh, is made of wires 0.001 to 0.003 inch in diameter (about 0.065 mm.). It becomes more efficient with use and at the same time shows a change to a very rough surface. The efficiency of conversion may reach 95 per cent of the ammonia. It has recently been discovered that platinum alloyed with a little rhodium is more efficient and lasts longer. Most of our nitric acid is now made by the ammonia oxidation process.

Properties of Nitric Acid.—The anhydrous nitric acid is a colorless liquid with a density of 1.52 and a boiling point of 86°. As stated before, it slowly decomposes and develops a red-brown color from dissolved oxides of nitrogen.

Nitric acid is a "strong" acid, ionizing freely, and is somewhat unstable. As a powerful oxidizing agent it is most interesting.

1. *Action on Non-metals.* Glowing carbon continues to burn in concentrated nitric acid:

$$4\,HNO_3 + C \longrightarrow 4\,NO_2 + CO_2 + 2\,H_2O.$$

Sulfur heated with nitric acid is oxidized to the trioxide and in the presence of water to sulfuric acid. In fact by this treatment combined sulfur is torn out and converted into sulfuric acid. This is the basis of quantitative methods of determining the percentage of sulfur in ores and in some foods.

2. *Action on Metals.* Very active metals displace hydrogen from this acid, but in most cases the hydrogen displaced is instantly oxidized by the acid and none escapes.

Less active metals, such as copper, are first converted into the oxide by the acid, which then dissolves the oxide. If it were not for this preliminary oxidation, nitric acid could not possibly attack metals below hydrogen in the electromotive series.

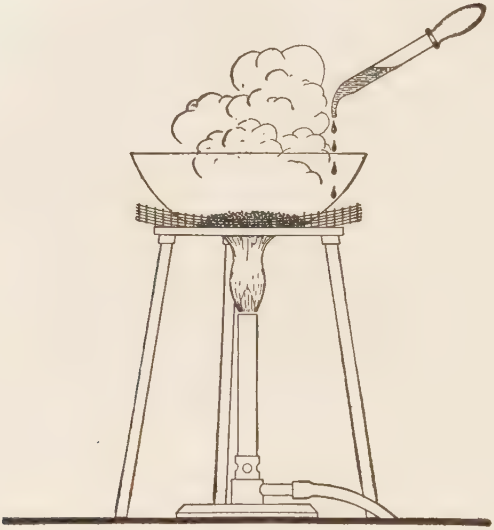


FIG. 103.—When a few drops of concentrated nitric acid are dropped on hot, slightly charred sawdust, the increased velocity of oxidation results in flame.

3. ***Action on Metallic Oxides.*** Oxides react readily with nitric acid, forming water and nitrates. Other reactions of interest follow:

$$CuO + 2\,HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O,$$
$$Cu(OH)_2 + 2\,HNO_3 \longrightarrow Cu(NO_3)_2 + 2\,H_2O,$$
$$CuCO_3 + 2\,HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O + CO_2.$$

4. ***Action on Organic Compounds.*** Cellulose (of cotton or wood) is attacked with formation of cellulose nitrates, some of which are high explosives. With glycerine a similar product called *nitroglycerine* is produced. Toluene yields the famous T.N.T. (*trinitrotoluene*) and even starch is nitrated to form a powerful explosive. Yellow stains on the hand may be due to the xanthoproteic acid formed by nitric acid reacting with protein tissue. Further discussion of nitration is found on page 341.

Nitro Compounds and Organic Nitrates.—Concentrated nitric acid reacts with organic compounds in two ways as well illustrated by reaction with glycerine and with benzene.

$$\text{Glycerine } C_3H_5 \boxed{(OH)_3 + 3\ H}\ NO_3 \longrightarrow 3\ H_2O + C_3H_5(NO_3)_3.$$

The product, $C_3H_5(NO_3)_3$, is wrongly called "nitroglycerine." The NO_3 group is present so the correct name is glyceryl trinitrate. The reaction includes the union of OH groups of the glycerine with H groups of the acid.

Dynamite is essentially a solid mixture of nitroglycerine with wood meal or infusorial earth but the mixture usually includes nitrates of sodium or ammonium. The thawing out of frozen dynamite is dangerous so nitrated glycol is commonly added to lower the freezing point of the nitroglycerine content of the dynamite.

Gelatin dynamite contains both nitroglycerine and "nitrocotton."

$$\text{Benzene, } C_6H_5 \boxed{H + HO}\ NO_2 \longrightarrow H_2O + C_6H_5NO_2.$$

Here it is the benzene, C_6H_6, that furnishes the H, and the nitric acid (written above as $HO \cdot NO_2$ for convenience) that furnishes the OH group for reaction to yield water. The product, $C_6H_5 \cdot NO_2$, is clearly not a nitrate of any sort, but, since it contains the nitro group—NO_2, must be called nitrobenzene. Cellulose contains OH groups and hence reacts like glycerine. Toluene $C_6H_5 \cdot CH_3$, resembles benzene closely and reacts similarly with nitric acid. These two type reactions are of vast importance as will be further shown in the chapter on cellulose.

Oxidation by Nitric Acid.—In the presence of a reducing agent dilute nitric acid breaks up, yielding (to the reducer) three oxygen atoms for every two molecules of the acid:

$$2\ HNO_3 \longrightarrow H_2O + 2\ NO + (3\ O).$$

The (O) of the above equation is not set free as oxygen gas but is merely used for convenience in balancing equations.

If sulfurous acid were the reducing agent, each molecule could take up one oxygen atom, forming sulfuric acid. Therefore the two nitric acid molecules are capable of taking care of three molecules of sulfurous acid:

$$2\ HNO_3 + 3\ H_2SO_3 \longrightarrow H_2O + 2\ NO + 3\ H_2SO_4.$$

Ferrous sulfate is oxidized by nitric acid as shown by the usual by-product, nitric oxide. The ferrous sulfate becomes ferric sulfate, with an increase in valence of the iron:

$$Fe^{++}SO_4 \longrightarrow Fe_2^{+++}(SO_4)_3.$$

This extra sulfate radical (SO_4) is obtained from some free sulfuric acid present.

Here we introduce a broader conception of oxidation. In the above reactions nitric acid caused the valence of iron to increase from two to three. The oxygen from the nitric acid did not actually add on to the ferrous sulfate, but it was used indirectly. So we may say that ***oxidation is an increase in valence of the positive or central element in a compound.*** It is noteworthy that the nitrogen in nitric acid has a positive valence of five as evident from the formula of its anhydride, N_2O_5, Yet after nitric acid has oxidized ferrous sulfate or other substances, the nitrogen appears as NO, where its positive valence must be two. Thus when nitric acid is itself reduced, its central element drops in positive valence from five to two. So we may say that ***reduction is a decrease in valence of the positive or central element.***

$$N_2O_5(N^{+++++}) \longrightarrow NO(N^{++}).$$

Drop in valence is 3. We spoke of nitric acid being reduced to nitric oxide. Activation of escaping hydrogen by a metal surface such as zinc carries the reduction, the lowering of valence of nitrogen, still farther. All of the oxygen is torn away from nitrogen by the active hydrogen and then hydrogen begins to add on. That is why ammonia may be formed with zinc and very dilute nitric acid but not with copper.

Depending upon the power of the reducing agent HNO_3 may be reduced as in the series

$$\overset{+5}{HNO_3} \longrightarrow \overset{+4}{NO_2} \longrightarrow \overset{+3}{HNO_2} \longrightarrow \overset{+1}{N_2O} \longrightarrow \overset{0}{N_2} \longrightarrow \overset{-3}{HN_3}.$$

Between the ends of this series nitrogen may change from a positive valence of 5 to a negative valence of 3 (in NH_3).

$$\begin{aligned} 8\,HNO_3 + 4\,Zn &\longrightarrow 4\,Zn(NO_3)_2 + (8\,H) \\ (8\,H) + HNO_3 &\longrightarrow NH_3 + 3\,H_2O \\ NH_3 + HNO_3 &\longrightarrow NH_4NO_3 \\ \hline \text{Adding, } 10\,HNO_3 + 4\,Zn &\longrightarrow NH_4NO_3 + 4\,Zn(NO_3)_2 + 3\,H_2O \end{aligned}$$

When concentrated acid is used, nitric oxide cannot be a product. It would be oxidized to nitrogen dioxide by the rest of the concentrated acid.

$$2\,HNO_3 \longrightarrow H_2O + 2\,NO_2 + (O).$$

Nitric acid oxidizes sulfur to sulfuric acid, iodine to iodic acid, powdered carbon to carbon dioxide, and red phosphorus to phosphoric acid.

Note again the difference in the oxidizing power of diluted and of concentrated nitric acid as shown towards metallic copper.

Diluted, $8\,HNO_3 + 3\,Cu \longrightarrow 3\,Cu(NO_3)_2 + 4\,H_2O + 2\,NO,$
Concentrated, $4\,HNO_3 + Cu \longrightarrow Cu(NO_3)_2 + 2\,H_2O + 2\,NO_2.$

Since nitric acid is such a powerful oxidizing agent, it can readily be reduced. However, a stream of hydrogen gas has no effect on it. If the hydrogen is generated in the vessel containing the nitric acid, reduction occurs. Perhaps this is because the atoms of hydrogen are especially active due to the catalytic influence of the metal displacing the hydrogen. Active hydrogen reduces nitric acid down to ammonia.

Exercise 1.—Add a few drops of nitric acid to a beaker filled with foam because of the action of zinc on dilute sulfuric acid. The escape of hydrogen is checked. Pour off the liquid, neutralize with sodium hydroxide, and smell the ammonia released. Explain with all equations.

Electronic Balancing of Equations.—As an option in balancing these oxidation-reduction equations we may consider again (review p. 181) Brinkley's method. Represent electrons by $(-)$.

(1) $HNO_3 + Cu \rightarrow Cu(NO_3)_2 + NO + H_2O$ (Unbalanced),
(2) $HNO_3 \rightarrow NO;\quad N^{+++++} \rightarrow N^{++}$ Gain, 3 $(-)$,
(3) $Cu \rightarrow Cu(NO_3)_2;\quad Cu^{\circ} \rightarrow Cu^{++}$ Loss, 2 $(-)$.

The oxidation-reduction ratio is, therefore,

$$2\,HNO_3 \text{ to } 3\,Cu.$$

But the 3 Cu^{++} ions require 6 extra NO_3^- ions to form 3 $Cu(NO_3)_2$ a compound that may be proved (by analysis) to exist in the products of equation (1). Therefore:

$$8\,HNO_3 + 3\,Cu \rightarrow 3\,Cu(NO_3)_2 + 2\,NO + 4\,H_2O.$$

By this method there must be an equal number of electrons $(-)$ gained and lost by the oxidizing and reducing agents. In this instance copper acts as a reducing agent for its valence is raised from zero to two.

The valence of nitrogen in HNO_3 must be five because the anhydride is N_2O_5.

Nitrous Acid, HNO_2.—When nitrogen trioxide or a mixture of nitric oxide and nitrogen dioxide is passed into cold water, nitrous acid is formed. Hence N_2O_3 is the anhydride of nitrous acid, as N_2O_5 is the anhydride of nitric acid:

$$N_2O_3 + H_2O \longrightarrow 2\,HNO_2.$$

The acid is quite unstable, even in solution. When nitrous acid is released from its salts by addition of sulfuric acid, red-brown fumes are seen (unless a great excess of water is present). As stated before, nitrogen dioxide in cold water yields both nitric and nitrous acids. There is a growing demand for nitrous acid in making organic dyes. Of course it is made and transported as sodium nitrite ($NaNO_2$), on account of the instability of the free acid, and mixed with sulfuric acid as used.

Nitrates and Nitrites.—The natural deposits of nitrates are mentioned on page 332.

All nitrates are soluble except those of mercury (divalent) and bismuth, which are hydrolyzed with formation of insoluble basic salts. However, they are soluble in the presence of nitric acid.

Nitrates are grouped in three classes according to their decomposition on heating:

$$\begin{aligned}
&(1)\quad NH_4NO_3 \longrightarrow 2\,H_2O + N_2O,\\
&(2)\quad NaNO_3 \longrightarrow NaNO_2 + O,\\
&(3)\quad 2\,Cu(NO_3)_2 \longrightarrow 2\,CuO + 4\,NO_2 + O_2.
\end{aligned}$$

Ammonium nitrate is the only member of the first group. Potassium nitrate acts like sodium nitrate. Practically all other nitrates decompose like copper nitrate.

Lead is sometimes fused with sodium nitrate to aid in the removal of oxygen. The resulting nitrite is dissolved and filtered from the insoluble lead oxide formed:

$$NaNO_3 + Pb \longrightarrow PbO + NaNO_2.$$

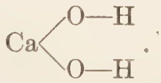
The Brown-Ring Test for Nitrates.—A very delicate test for nitrates (and nitrites) makes use of the formation of the brown compound $FeSO_4 \cdot NO$. To the suspected nitrate a solution of ferrous sulfate is added and then, while inclining the tube, concentrated sulfuric acid is carefully poured down the wall of the tube so two layers form. At the junction of the two layers a brown ring appears if a nitrate is present. The sulfuric acid liberates nitric acid from any nitrate, which in turn oxidizes some ferrous sulfate. The nitric oxide by-product combines with some remaining ferrous sulfate to form brown $FeSO_4 \cdot NO$.

Addition of dilute sulfuric acid to a suspected nitrate or nitrite enables one to distinguish between the two (unless a large amount of water is present). Red-brown oxides of nitrogen escape from the nitrite, but not from the nitrate.

Structural Formulas.—Nearly all acids are made up of hydroxide groups united with a non-metal, such as nitrogen or sulfur. This is not to be confused with the fact that bases are compounds of the hydroxide group with metals. The difference is that in water solution bases yield OH^- ions, while acids yield H^+ ions.

The structural formula of bases is simple.

$\mathrm{K{—}O{—}H}$ $\mathrm{Na{—}O{—}H}$

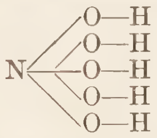


$$\mathrm{Ca}\begin{array}{l}\diagup\mathrm{O{—}H}\\ \diagdown\mathrm{O{—}H}\end{array}.$$

With hydroxy acids a clear conception of structure may be obtained by considering that the acid is derived from a parent acid in which the non-metal holds as many —OH groups as indicated by its valence. This makes it essential to learn the correct valence of the central element. In nitric acid we learn this by noting the formula of the anhydride. The nitrogen is pentavalent:

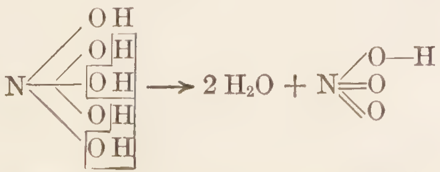
$$2\,HNO_3 \longrightarrow H_2O + N_2O_5.$$

Consequently a parent acid may be represented thus:



$$\mathrm{N}\begin{array}{l}\mathrm{O{—}H}\\ \mathrm{O{—}H}\\ \mathrm{O{—}H}\\ \mathrm{O{—}H}\\ \mathrm{O{—}H}\end{array}$$

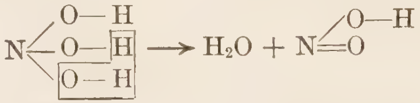
This H_5NO_5 is not at all imaginary. Erdmann (*Zeit. f. anorg. Chem.* 31–32, 431, 1902) made it in the form of long needles melting at 35°. To change from this to the ordinary HNO_3 calls for the spontaneous breaking off of $2\,H_2O$. In the diagram the second —OH has lost its hydrogen.



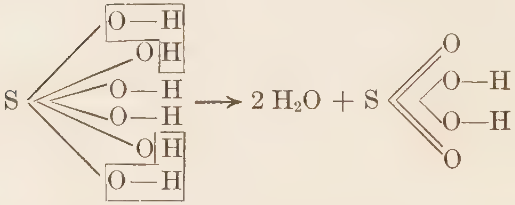
Parent Acid Nitric Acid

But oxygen is divalent, so the bond of valence once used to hold the hydrogen must exert itself towards something. This suits nitrogen, for its bond of valence previously occupied in holding the third —OH can extend its force to the second oxygen. The same reasoning applies to the fourth and fifth groups. This explains the two double-bonded oxygen atoms. Loss of water is neither oxidation nor reduction, so the valence of the nitrogen remains five and the valence of oxygen two.

In nitrous acid the valence of nitrogen is three ($2HNO_2 \longrightarrow H_2O + N_2O_3$). So the structure is evident. Nor is there any difficulty with sulfuric acid ($H_2SO_4 \longrightarrow H_2O + SO_3$):



Parent Acid Nitrous Acid



Parent Acid Sulfuric Acid

With some acids the parent acid actually exists, as H_4SiO_4, but with others it is merely an imaginary compound. However, if it helps clarify our ideas of structure it is well worth using.

EXERCISES

2. What volume of sulfuric acid having a specific gravity of 1.83 (94 per cent H_2SO_4) will be required to convert 7.5 Kg. of sodium nitrate (80 per cent pure) into nitric acid?

3. How many grams of nitric acid will be prepared in the above reaction?

4. Assuming a 95 per cent yield, how much Chili saltpeter, 90 per cent pure, would be required to prepare 800 Kg. of 68 per cent nitric acid?

5. Develop the structural formula of permanganic acid, $HMnO_4$, and of dichromic acid, $H_2Cr_2O_7$.

6. Draw a "Nitrogen Tree" somewhat like the "Oxygen Tree" on page 37.

7. What possible connection is there between oil shales and fertilizers?

8. What is the chief cost in making ammonia directly from hydrogen and nitrogen?

9. What process of nitrogen fixation will dominate the field?

10. How could you dry ammonia?

11. Compare the action of nitric acid on metals above hydrogen in the electromotive (or activity) series with the action on metals below hydrogen.

12. How useful would the Haber process be without the Ostwald process?

13. How can you tell the difference between a nitrate and a nitrite?

14. How does the fact that cotton can be nitrated touch your own personal safety, comfort, pleasure, or appearance?

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✓

CHAPTER XXVIII

THE PHOSPHORUS GROUP

Elements	Atomic Weight	Density of Solid	Melting Point	Color of Solid	Hydroxides are
Nitrogen	14.08	1.0265	−210.5°	White	Strongly acidic
Phosphorus	31.04	1.83	44.10	White	Moderately acidic
Arsenic	74.96	5.73	Sublimes	Gray	Moderately acidic
Antimony	120.2	6.62	630	Silver-white	More basic than acidic
Bismuth	208.0	9.80	269	Reddish-white	Weakly basic

A glance at the Periodic Table shows that the five elements listed above resemble each other in properties. Their place in the table calls for valences of three and five, and these are common except with bismuth, which practically limits itself to a valence of three. With increasing atomic weights these five elements become more metallic, with all that such a change involves. This change to the basic nature is still more marked with antimony and is complete with bismuth.

The predominant valences of three and five produce a striking similarity in the formulas of compounds. It will pay the student to compare each point brought out for one of the elements with similar facts for the other elements.

All the hydrides are gases, like ammonia, although the others do not react with water to form bases. All the chlorides, or other halides, are hydrolyzed by water, yielding hydroxides which are more or less acidic. Most of the metallic compounds react with water to form the hydrides.

Phosphorus

History.—The discovery of phosphorus was an accident. Brandt, a German alchemist, was searching for the Philosopher's Stone with which he could transform silver into gold. In 1669 he ignited dried urine with charcoal in a clay retort and secured a new substance that astonished him. It glowed in the dark when exposed to the air, hence the name given it—phosphorus (bearer of light).

Occurrence.—The element is too active chemically to be found free, but as phosphorite ($Ca_3(PO_4)_2$), a fossil deposit, it is plentiful in the United States and North Africa. Apatite ($3\ Ca_3(PO_4)_2 \cdot CaF_2$), a primitive rock, occurs in large deposits in Canada. Some iron ores contain very appreciable amounts of phosphates. The average human skeleton contains 1400 g. of phosphorus, muscle 130 g. and brain-nerve 12 g. The hard part of bones is calcium phosphate, and organic phosphorus compounds are found in nerve tissue, muscles, and the germs of seeds. Consequently the element is essential to animal and plant growth. Egg-yolk and beans are especially rich in organic phosphorus compounds, but peas and whole wheat are also valuable sources. The average human body contains 1.5 K. of combined phosphorus. Since it is a part of plant and animal tissue, it is evident that all fertile soils must contain phosphates.

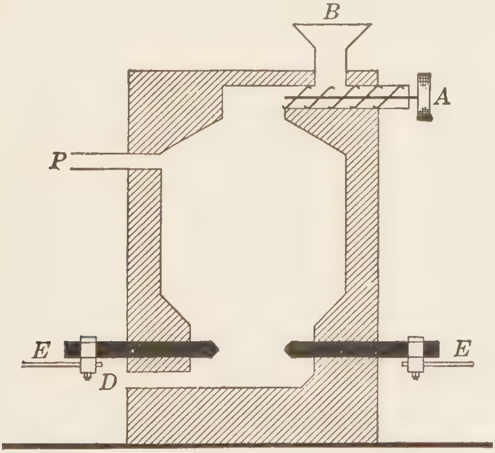


Fig. 104.—Phosphorus furnace.

Preparation.—The modern method of preparing phosphorus is to heat phosphate rock with sand and coke in the electric furnace (Fig. 104). The charge enters the furnace from *B* by the worm feed *A*:

$$2\ Ca_3(PO_4)_2 + 6\ SiO_2 + 10\ C \longrightarrow 6\ CaSiO_3 + 10\ CO + P_4.$$

The phosphorus distills off at *P* and is condensed in cold water. After filtering it is molded into small sticks and kept under water.

Exercise 1.—Why not heat phosphate rock, sulfuric acid, and coke together to make phosphorus cheaply?

Properties.—Phosphorus exists in at least two allotropic forms, white and red, reminding us of oxygen—ozone and the different forms of sulfur.

White Phosphorus.—White phosphorus is a translucent, waxy solid, melting at 44° and boiling at 287°. Its density is 1.83 at room temperature. From the density of its vapor it is found that up to 1500° the molecule is P_4 and at 1700° it is P_2. Insoluble in water, it is readily soluble in carbon disulfide, turpentine, ether, olive oil, and other liquids. From these solvents it crystallizes in the regular system. It is extremely active, combining with many elements. In warm air it ignites (at about 35°) so it is always kept under water. The heat of the hand is sufficient to ignite it and serious burns may result. This form of the element is very poisonous, a fatal dose being only 0.15 g.

Exercise 2.—What was said about phosphorus in connection with ozone and also in connection with iodine?

Red Phosphorus.—When white phosphorus is heated without access of air to 230°–300° it changes to the red modification, more rapidly in the presence of a trace of iodine as a catalyst. The same change is observed on the surface of sticks of the white variety on long exposure to light. This explains the common term, "yellow phosphorus." When the red form is distilled the vapors condense to the usual white form.

The transformation from white to red involves a change in specific gravity from 1.83 to about 2.34 and as much heat is liberated, there must be less energy in the red form. This explains why the heat of combustion of the red phosphorus is less. On burning, each variety produces a dense white smoke of solid particles of the pentoxide. Red phosphorus is not soluble in any solvent, is non-poisonous and must be heated to about 240° before it takes fire. It is microcrystalline.

Phosphorus crystallized from molten lead is black and metallic in appearance.

Matches.—The outstanding use of the element has always been in the manufacture of matches. To be accurate it was in 1827 that friction matches came into general use. Until recent years the match head contained white phosphorus, an oxidizing agent such as manganese dioxide, potassium chlorate or potassium nitrate, and glue. The glue, although primarily used as an adhesive, protected the phosphorus from oxidation until the heat of friction caused it to unite almost explosively with the oxygen of the potassium chlorate. The match sticks had been dipped in melted paraffin, which after ignition of the phosphorus readily took fire and then ignited the wood. However, the workers in match factories developed horrible diseases of the bones due to constant exposure to the vapors of phosphorus. For this reason one after another of the great nations forbade the use of this element until in 1913 the United States joined this humane crusade by placing a prohibitive tax on matches made by the old

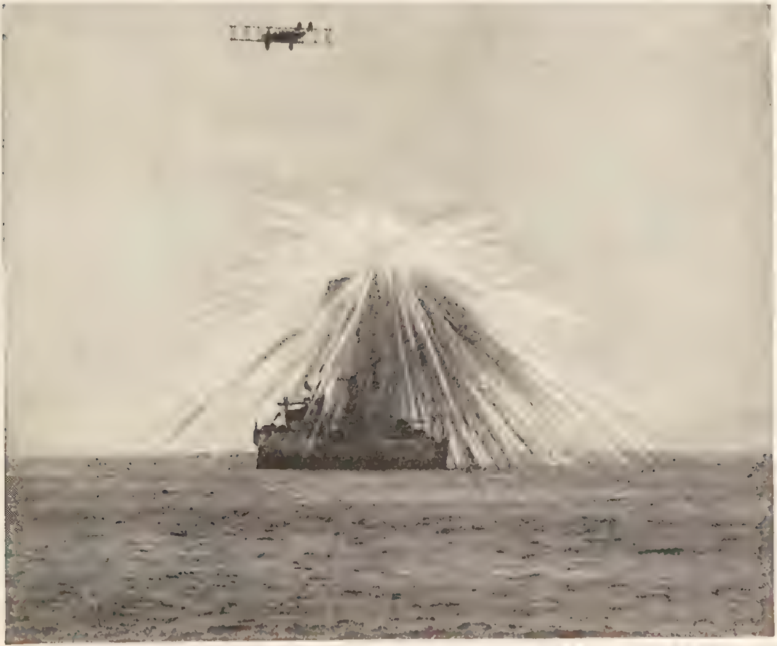


FIG. 105.—An airplane makes a direct hit with a 100-pound phosphorus bomb on a discarded battleship.

method. Tetraphosphorus trisulfide (P_4S_3) was substituted. Although its odor is not exactly attractive, this sulfide is comparatively safe in manufacture and in use.

Safety matches are a special type that must be scratched on a special surface before they ignite. The head contains no phosphorus compound at all. Antimony trisulfide (Sb_2S_3) is the combustible material mixed with glue (or dextrin) and the usual oxidizing agent, which may be red lead or potassium dichromate, instead of those mentioned before. The scratching surface on the box is a mixture of powdered glass for friction, glue, and red phosphorus.

Other Uses.—Most of the phosphorus produced goes into the match industry in the red form or as the sulfide. A small amount is used as a rat poison and during the World War much was used in incendiary grenades or bombs and in making smoke screens of the pentoxide.

Chlorides.—Phosphorus reacts with chlorine, even in the cold, to form the trichloride (PCl_3), a colorless fuming liquid of density 1.6, and the pentachloride (PCl_5), a pale yellow solid. Passing more chlorine through the trichloride converts it into the pentachloride, with evolution of much heat:

$$PCl_3 + Cl_2 \longrightarrow PCl_5.$$

By direct combination
with Cl_2
Control it by time

On attempting to get the melting point of the solid it dissociates. The equilibrium is, of course, influenced by temperature and pressure:

$$PCl_5 \rightleftarrows PCl_3 + Cl_2.$$

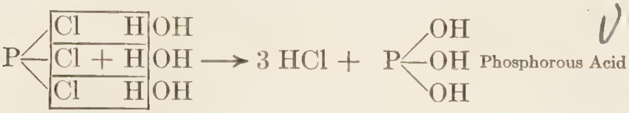
Heated in a closed tube the pressure of gases formed prevents further dissociation and the solid melts. Similar facts are true of ammonium chloride.

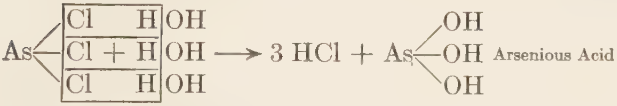
Exercise 3.—State the parallel facts for ammonium chloride.

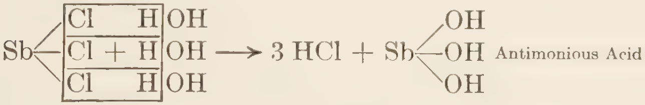
The most interesting thing about these chlorides of phosphorus is their hydrolysis by water, a fact which shows the relations between the acids. The other halides (all formed by direct union of the elements) are the trifluoride and pentafluoride (gases), the liquid tribromide, the solid pentabromide, and the solid iodides (P_2I_4 and PI_3).

The Acids of Phosphorus.—A study of the hydrolysis of the chlorides of phosphorus and of the other elements of the group is of the utmost importance in giving the student a clear conception of the formulas of the acids.

Valence 3


Phosphorous Acid


Arsenious Acid

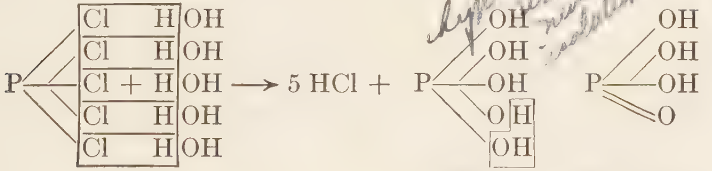

Antimonious Acid

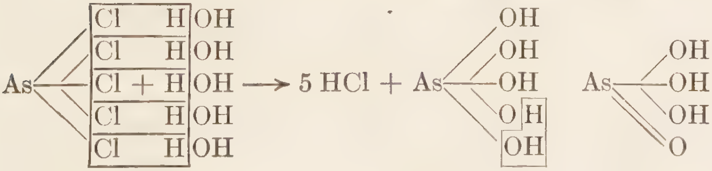
With $BiCl_3$ the hydrolysis is only partial, although the principle is the same. It will be given under Bismuth.

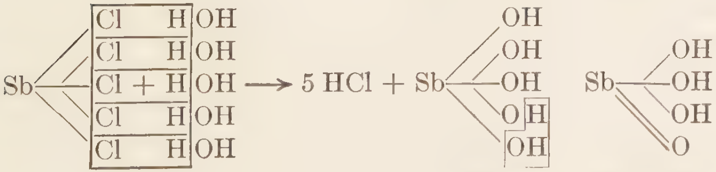
The reaction of water with the tribromides and triiodides is similar. Nitrogen trichloride is a dangerous explosive, so it need not be considered here.

Hypothetical intermediate never isolated.

Valence


Parent Phosphoric Acid
Orthophosphoric Acid


Parent Arsenic Acid
Orthoarsenic Acid


Parent Antimonic Acid
Orthoantimonic Acid

These parent acids have never been isolated so they exist for a brief instant if at all. However it is perfectly legitimate and immensely helpful to discuss their formulas as above. Their spontaneous loss of water yielding the familiar ortho acids reminds us of the explanation previously given of the structure of nitrous and nitric acids.

Orthophosphoric Acid.—All the acids of pentavalent phosphorus revert (by hydration) to orthophosphoric acid in aqueous solution. This acid can be made directly from the element by oxidation with nitric acid (***Caution!***). With white phosphorus the action may be explosive if acid of a greater specific gravity than 1.2 be used. Below that concentration the action is slow. On evaporation to a syrup which is held at 30° to 40°, colorless crystals (H_3PO_4) separate. The pure acid can also be made by reaction of water with phosphorus pentoxide. At first metaphosphoric acid (HPO_3) forms but slowly, or more rapidly if a little nitric acid is added as a catalyst; this acid adds more water, and the orthophosphoric acid (H_3PO_4) results. In other words the pentoxide is the anhydride of this acid:

$$P_2O_5 + H_2O \longrightarrow 2\ HPO_3,$$
$$P_2O_5 + 3\ H_2O \longrightarrow 2\ H_3PO_4.$$

The commercial acid, a thick syrupy liquid of about 85 per cent concentration, is cheaply made from phosphate rock:

$$\left[Ca_3(PO_4)_2 + 3\ H_2SO_4 \longrightarrow 3\ CaSO_4 + 2\ H_3PO_4.\right]$$

EXERCISE 4.—If in the above reaction two-thirds as much sulfuric acid were used, what would be the product? Its uses?

Since 1920 the "thermal" process has been developed by which silica instead of sulfuric acid is used to displace the phosphoric acid from its calcium salt. The high temperature of the electric furnace is used to bring about this reaction. Coke is added to the charge just as in the manufacture of free phosphorus. The reducing power of the hot coke helps to break down the calcium phosphate by pulling out some of the oxygen while the sand pulls out calcium oxide, forming calcium silicate. The phosphorus released is finally burned to P_2O_5 in an excess of air and it is a simple matter to treat with water, thus securing the acid, H_3PO_4. It has been suggested that the reactions are as follows:

$$\begin{array}{ll}
(1) & 2\,Ca_3(PO_4)_2 + 10\,C \longrightarrow 6\,CaO + 10\,CO + P_4, \\
(2) & CaO + SiO_2 \longrightarrow CaSiO_3, \\
(3) & P_4 + 5\,O_2 \longrightarrow 2\,P_2O_5, \\
(4) & P_2O_5 + 3\,H_2O \longrightarrow 2\,H_3PO_4, \\
(5) & 2\,CO + O_2 \longrightarrow 2\,CO_2.
\end{array}$$

The cost of electric furnace heating will probably hold back the application of this process to the fertilizer industry. Furnaces heated more cheaply by oil, powdered coal, or the like will, doubtless, come into use for this process.

It has been observed that when chemically pure tricalcium phosphate was ignited for one hour at 1300° C., with or without silica added, very little, if any phosphorus volatilized. When the phosphate was mixed with one-fifth of its weight of pure carbon, however, and the mixture heated as before under reducing conditions in a graphite container, about 45 per cent of the phosphorus escaped from the charge. At a temperature of 1400° C. the volatilization of phosphorus was increased to 96 per cent of the total present, and was complete at 1550° C. The addition of both sand and carbon to the phosphate had a still more marked effect on the evolution of the phosphorus. Thus, in a mixture of phosphate rock, silica, and carbon containing three molecular equivalents of lime to one of silica, the evolution of phosphorus in a reducing atmosphere amounted to 96 per cent at 1300° C.

Phosphoric acid or its salt is used in the preparation of fertilizer, in baking powder, water softening, weighting silk, clarifying sugar solutions, rust-proofing of metal, fire-proofing, soft drinks, and in yeast manufacture. Florida is the chief producing state, with Tennessee second.

Pyrophosphoric Acid.—This acid, as its name indicates, is the result of heating orthophosphoric acid. At 213° water is lost as follows:

$$2\,H_3PO_4 \longrightarrow H_2O + \underline{H_4P_2O_7}.$$

Metaphosphoric Acid.—By heating orthophosphoric acid to 400° a greater loss of water results than in the preparation of the pyro acid, and metaphosphoric acid is formed:

$$H_3PO_4 \longrightarrow H_2O + \underline{HPO_3}.$$

It is also the first reaction product when the pentoxide is added to water. The pure dry acid looks like ice and is called "glacial" phosphoric acid. Like the ortho and pyro acids, it is soluble in water. It can be volatilized at a red heat.

Salts.—From the formula H_3PO_4 three types of salts are to be expected, and they are known. The sodium salts illustrate the relations:

Na_3PO_4, trisodium phosphate (the tertiary salt),
Na_2HPO_4, disodium phosphate (the secondary salt), [illegible]
NaH_2PO_4, monosodium phosphate (the primary salt).

The ***trisodium phosphate*** is hydrolyzed to a powerfully alkaline solution and so is often used as a washing powder. The salt is easily prepared by adding sodium hydroxide in large excess to the acid. Thus:

$$H_3PO_4 + 3\ NaOH \rightleftarrows Na_3PO_4 + 3\ H_2O.$$

The tendency towards reversal is here so great that it is only by the mass action of a large excess of the base that crystals of the trisodium phosphate can be secured. Heavy metals like lead form only tertiary phosphates. ***Trisodium phosphate*** is much used as a cleansing powder.

If phosphoric acid is titrated with sodium hydroxide until neutral to phenolphthalein as an indicator, ***disodium phosphate*** is formed. This is the "sodium phosphate" of the side shelf and is important also in the silk industry.

$$H_3PO_4 + 2\ NaOH \longrightarrow Na_2HPO_4 + 2\ H_2O.$$

The ***monosodium phosphate,*** which is used in baking powders, is prepared from an equimolecular mixture of the acid and the base:

$$H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O.$$

Its solution is weakly acidic.

The acidic or basic reactions of the orthophosphates should be evident from a comparison of the ionization constants (p. 355) of orthophosphoric acid in its three stages.

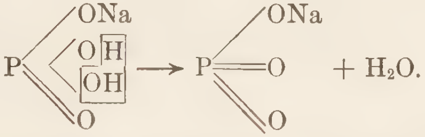
$$(1) \qquad \frac{[H^+] \times [H_2PO_4^-]}{[H_3PO_4]} = 10^{-2}$$

$$(2) \qquad \frac{[H^+] \times [HPO_4^{--}]}{[H_2PO_4^-]} = 10^{-7}$$

$$(3) \qquad \frac{[H^+] \times [PO_4^{---}]}{[HPO_4^{--}]} = 10^{-13}$$

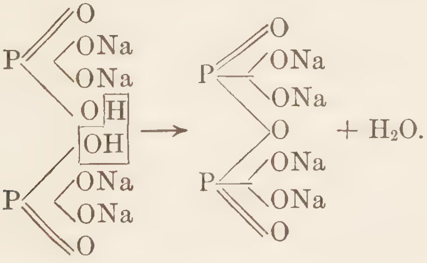
NOTE: 10^{-7} is really $\frac{1}{10^7}$ or 0.000,000,1.

Interesting changes take place on heating the dry salts. If there are two —OH groups in one molecule, they yield a molecule of water. If only one —OH is found in a molecule of the salt, then two molecules must get together in order to make the loss of water possible:



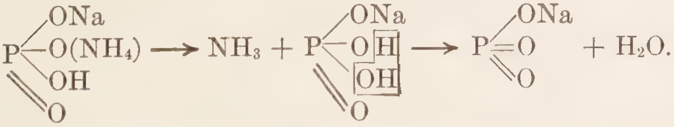
NaH_2PO_4, monosodium phosphate ⟶ $NaPO_3$, sodium metaphosphate, and water.

Here an orthophosphate is changed into a metaphosphate. By adding an acid the free phosphoric acids could be obtained.



2 Na_2HPO_4, disodium phosphate ⟶ $Na_4P_2O_7$, ***sodium pyrophosphate*** and water.

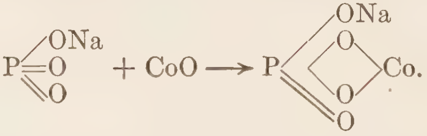
Here an orthophosphate is changed into a pyrophosphate.



$Na(NH_4)HPO_4$, microcosmic salt ⟶ NaH_2PO_4 ⟶ $NaPO_3$.

Here an orthophosphate is changed to a metaphosphate.

"Microcosmic salt" is used in bead tests to detect the presence of certain salts. When heated in a loop of platinum wire the salt loses water of crystallization and then ammonia gas. This loss of NH_3 leaves an extra —OH group, and further heating, now that there are two such groups, means the loss of a water molecule as diagrammed above. A metaphosphate results. The glassy bead is then touched to the substance to be tested and heated again. If a cobalt salt is tested, some oxide is probably formed by the hot flame, and this oxide unites directly with the sodium metaphosphate of the bead to form an orthophosphate of sodium and cobalt. This is intensely blue and is characteristic of cobalt, hence a test for it. Compare the structure of the blue compound with that of orthophosphoric acid. One hydrogen atom is replaced by a sodium atom and two hydrogen atoms by one of cobalt:



Exercise 5.—Start with the element and show how to make from it all three acids of pentavalent phosphorus.

Exercise 6.—Start with phosphorus pentoxide and make an orthophosphate. From this make a metaphosphate. From this make an orthophosphate again.

Our annual production of the various sodium phosphates now totals 170,000,000 pounds.

Tests for the Different Phosphates.—A neutral solution of an orthophosphate reacts with silver nitrate to form yellow silver phosphate.

White precipitates of silver pyrophosphate and silver metaphosphate leave us uncertain as to which salt we are testing. However, a solution of egg albumin is coagulated by metaphosphoric acid, while the other acids have no such effect. Note that the tests with silver nitrate must be made on solutions of the salts, and that the albumin test must be made with the free acids. If salt solutions are at hand, addition of acetic acid will liberate enough of the phosphoric acids. Nitric acid solutions of orthophosphates form a yellow precipitate when warmed with ammonium molybdate. The formula is too intricate for us in this year's work. With magnesia mixture a white precipitate of magnesium ammonium phosphate ($MgNH_4PO_4$) forms. These two reactions are the basis of the best methods of quantitatively determining the phosphorus in fertilizers, etc. Precipitates of exactly the same appearance and similar formula are obtained with orthoarsenates.

The Oxides.—The pentoxide, P_2O_5, is obtained by burning the element with free access of air. It is a white solid which reacts rather violently with water to form first, metaphosphoric, and finally orthophosphoric acid and so must be their anhydride. Its affinity for water is so great that it is the most powerful drying agent known, though not the cheapest. When phosphate rock is heated with sand in the electric furnace the pentoxide is volatilized. These white fumes can be captured by the Cottrell electric precipitation process. The charged dust particles are discharged by a high-potential plate, and then collected as so much dust. Dust in any industry, in an iron furnace or a cement mill, or even sulfuric acid mist may be recovered in this way.

The trioxide (P_2O_3 or P_4O_6) is formed when the element is burned without enough oxygen to form the pentoxide. It is a white solid which can readily be separated from the less volatile pentoxide by heating to 173.1°, its boiling point.

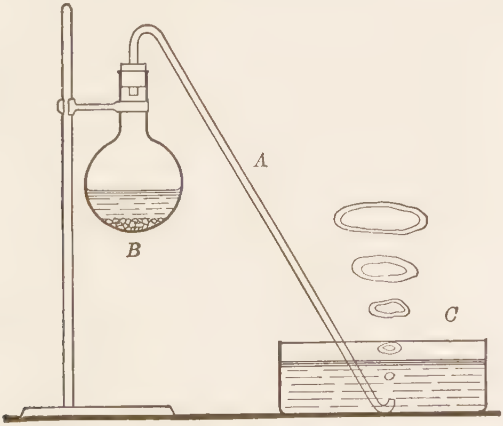


Fig. 106.—Phosphine smoke rings.

Phosphine.—Phosphine (PH_3) reminds us of ammonia in formula and in its gaseous nature, but does not react with water to form a base.

Phosphine is a very poisonous gas often spoken of as spontaneously inflammable. However, pure phosphine must be ignited before it burns. In the usual method of preparing it a liquid impurity, P_2H_4, which itself takes fire on contact with the air, ignites the phosphine. This burns, forming white clouds of the pentoxide. When the gas bubbles through water beautiful smoke rings are formed if the air in the room is quiet.

In the flask *B* (Fig. 106) white phosphorus is heated with a concentrated solution of potassium hydroxide. In order that no oxygen may be present in the flask a stream of ordinary illuminating gas is led through *A* for a minute or two. This sweeps out air from the flask. On heating, the phosphorus melts and the reaction begins. *C* is a wide dish of water:

$$4\ P + 3\ KOH + 3\ H_2O \rightarrow PH_3 + 3\ KH_2PO_2.$$

Phosphine is also prepared by the action of water on phosphides. This is very similar to the formation of ammonia by the action of water on a nitride:

$$Ca_3P_2 + 6\ H_2O \rightarrow 2\ PH_3 + 3\ Ca(OH)_2,$$
$$Mg_3N_2 + 6\ H_2O \rightarrow 2\ NH_3 + 3\ Mg(OH)_2.$$

Phosphate Fertilizers.—Since plants contain phosphorus compounds, soils must contain phosphates or must be fertilized properly. Although most fertile soils actually contain such compounds, heavy cropping finally exhausts the supply and phosphates must be added. Of course plants can utilize only soluble phosphates, so the common practice is to treat ground calcium phosphate rock with enough sulfuric acid to form the soluble primary calcium phosphate (only one hydrogen of each molecule of the acid replaced by a metal), or as it is called commercially, "superphosphate":

$$Ca_3(PO_4)_2 + 2\ H_2SO_4 \longrightarrow Ca(H_2PO_4)_2 + 2\ CaSO_4.$$

When the new "thermal" process of making phosphoric acid (page 357) becomes cheap enough it may displace sulfuric acid in the preparation of superphosphate. Ground rock would then be treated directly with free phosphoric acid:

$$Ca_3(PO_4)_2 + 4\ H_3PO_4 \longrightarrow 3\ Ca(H_2PO_4)_2.$$

To save freight rates ammonium phosphate and potassium phosphate will be prepared and mixed with fillers near the place where the fertilizer is to be used.

In recent years farmers have learned that ground phosphate rock plowed under with a green forage crop or manure is made soluble in reasonable time by the acids of decaying organic matter. This ground rock is cheaper than superphosphate.

The world uses 10,000,000 tons of phosphate rock yearly and the United States usually produces about one-third of this total, in 1928 producing 3,400,000 tons. However, North Africa now surpasses the United States in production. Here is a strategic resource in a prolonged war, and in peace an economic bargaining weapon of great importance. Civilized nations must have phosphate rock. France is in control of most of the deposits that the United States does not own. In her colonies of Algiers and Tunis as well as in parts of Morocco are vast deposits. In America, Florida produces two-thirds of the present output, but Tennessee, South Carolina, and Montana also yield large amounts. The largest deposit in the world is found in Utah, Montana, Wyoming, and Idaho, where government investigations report at least 2,500,000,000 tons of 30 per cent calcium phosphate in sight. Since our Southern deposits will be exhausted in a century, it is reassuring to learn that this Western deposit will supply our needs for several centuries.

EXERCISE 7.—Would you expect to get hydrogen sulfide by treating phosphorus sulfides with dilute acids? Why?

Hydrogen by the Aid of Phosphorus.—It was demonstrated in a small European plant during 1929 that the phosphorus vapor (no air present) escaping from the furnace could be mixed with steam and passed over a catalyst at 700° C. with the following reaction:

$$\frac{P_4 + 16\ H_2O}{\text{catalyst at }700^\circ\text{ C.}} \rightarrow 4\ H_3PO_4 + 10\ H_2.$$

There is a troublesome side reaction by which PH_3 forms, but the method is attractive, for the free hydrogen could be purified, mixed with nitrogen, converted into ammonia (page 322), and the ammonia neutralized with the phosphoric acid just mentioned to form a remarkable, compact fertilizer, diammonium phosphate, $(NH_4)_2HPO_4$.

ARSENIC

History.—The alchemists were acquainted with arsenic and even the ancient Greeks knew some of its compounds. Albertus Magnus first prepared the element in the thirteenth century. Brandt (the discoverer of phosphorus) proved "white arsenic" to be a "calx" or ash of the element. After Lavoisier made clear the nature of oxidation this calx was recognized as the oxide.

Occurrence.—Arsenical pyrites or mispickel (FeAsS) is abundant, and there are also deposits of the trioxide, orpiment (As_2S_3), realgar (As_2S_2), and arsenides of iron, nickel, and cobalt. It occurs in some sulfide ores, such as those of copper, and thus its oxide is found in flue dust from the smelters. Canadian arsenic is chiefly derived from the silver-cobalt-nickel arsenides of the cobalt district.

Preparation.—Much arsenic is made commercially by heating arsenical pyrites:

$$4\ FeAsS \longrightarrow 4\ FeS + 4\ As.$$

In the laboratory, reduction of the trioxide by hot carbon is an easy method:

$$2\ As_2O_3 + 3\ C \longrightarrow 4\ As + 3\ CO_2.$$

Arsenides react with water or, more rapidly, with acids to form arsine. This is similar to the action of nitrides and phosphides on water:

$$Zn_3As_2 + 6\ HCl \longrightarrow 2\ AsH_3 + 3\ ZnCl_2.$$

The famous Marsh test for arsenic is based on reduction by active hydrogen. A flask (Fig. 107) containing a frothing mixture of pure zinc and sulfuric acid is connected with a glass tube constricted at two points. Through a funnel a solution of the suspected arsenic compound is added. The arsine formed by reduction is heated as it passes through the delivery tube and the element is deposited farther along as a shining mirror. It is best worked so that the mirror forms in a constriction. As little as one millionth of a gram of arsenic can be detected in this way, so it is a famous test in poisoning cases. An interesting variation is to light the hydrogen as it issues from the delivery tip and to hold a

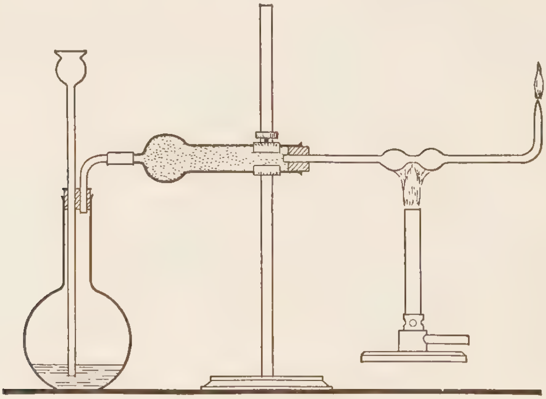


FIG. 107.—The Marsh test for arsenic.

porcelain dish in the flame. The heat of the flame decomposes arsine in the middle of the jet and a shining black spot of the element forms on the cold dish.

$$2\ AsH_3 \longrightarrow 2\ As + 3\ H_2. \quad \checkmark$$

A similar reaction occurs in the hydrogen sulfide flame (p. 237).

Properties.—In physical properties arsenic resembles the metals, but chemically it is a non-metal, an acid former. Like another member of this group, phosphorus, it exists in allotropic forms.

The common form is gray, brittle, has a specific gravity of 5.727, and volatilizes on heating. (When a solid passes into vapor without melting it is said to sublime.) Like other solids that sublime it can be melted under pressure. Sublimation affords an easy method of purifying. The vapors have a strong garlic odor. The element burns in air, forming a white smoke of the trioxide.

The element is used commercially in alloys as a hardening agent, notably in lead shot.

Oxides.—The trioxide (As_2O_3), a white powder, is the product of burning arsenic or its compounds. Hence it is found mixed with the flue dust of smelters. In the great copper smelter at Anaconda, Montana, this oxide is precipitated from the flue gases by high potential electric charges (75,000 volts). Great quantities are recovered. The United States uses 15,000 tons for insecticides, weed killers, sheep and cattle dips, preserving bird skins and furs, and in making opaque glass and enamels. It is an important ally of the farmer. Calcium arsenate is used in great quantities to kill the boll weevil which has threatened our cotton industry with destruction. In fact this is the chief use of arsenic. Paris green is another well-known arsenic compound.

The trioxide reacts to a slight extent with water to form arsenious acid and dissolves in hot water to a noticeable degree.

The pentoxide (As_2O_5) cannot be prepared by burning arsenic in plenty of air (like phosphorus pentoxide) but only by heating arsenic acid. It readily unites with water to form arsenic acid again.

The trioxide, erroneously termed "arsenic" by the public, has often been used as a poison. The antidote is freshly precipitated ferric hydroxide (lime water mixed with ferric chloride is a convenient household source).

In some mountainous districts "arsenic eaters" take as much as four times an ordinary "fatal dose" of the trioxide in order to increase the number of red blood corpuscles, strengthen their respiration and steady their nerves. The body gradually becomes accustomed to such doses.

Arsine.—Like the corresponding compound, phosphine, this gas is poisonous, only more so. It does not dissolve in water as does ammonia, nor does it form arsonium salts under any conditions. Arsine is readily formed by the action of active hydrogen on arsenic compounds:

$$As_2O_3 + 12\ H \longrightarrow 2\ AsH_3 + 3\ H_2O.$$

Acids of Arsenic.—As with nitrogen and phosphorus, so here we have two types of acids of arsenic, those of trivalent arsenic and those of pentavalent arsenic. The derivation and naming are similar.

As_2O_3 is the anhydride of arsenious acid (H_3AsO_3) and when dissolved in water is in equilibrium with the acid. That the acid is present in solution is evident from the weakly acid reaction and the formation of arsenites on addition of a base. Both acid and arsenites are good reducing agents.

Arsenic acid (H_3AsO_4) is formed by the oxidation of the trioxide with chlorine water or nitric acid:

$$H_3AsO_3 + Cl_2 + H_2O \longrightarrow 2\ HCl + H_3AsO_4.$$

Exercise 8.—Write the equations representing the action of nitric acid on arsenic trioxide.

Arsenic acid is a moderately strong acid, very soluble in water and ionizing in ways similar to phosphoric acid. Like that acid it yields a yellow precipitate on warming with ammonium molybdate and a white one ($MgNH_4AsO_4$) on treating with magnesia mixture.

The Sulfides.—Solutions of compounds of trivalent arsenic react with hydrogen sulfide to precipitate yellow arsenic trisulfide:

$$2\ AsCl_3 + 3\ H_2S \longrightarrow 6\ HCl + As_2S_3.$$

Compounds of pentavalent arsenic react slowly, even when kept almost boiling, to yield mixtures of yellow arsenic pentasulfide, trisulfide, and sulfur. Both sulfides are oxidized by hot concentrated nitric acid to arsenic acid with release of sulfur. With prolonged action the sulfur may become sulfuric acid.

The sulfides of the sodium group react with arsenic trisulfide to form soluble salts.

The Thio-Acids and Salts.—On warming arsenic trisulfide with sodium sulfide (ammonium sulfide is often used with similar results) a soluble salt is obtained. If sodium polysulfide (Na_2S_2) is used, a different soluble salt is obtained:

$$\left\{\begin{array}{l} As_2S_3 + 3\ Na_2S \longrightarrow 2\ Na_3AsS_3, \text{ sodium thioarsenite,} \\ As_2S_3 + 3\ Na_2S_2 \longrightarrow 2\ Na_3AsS_4 + S, \text{ sodium thioarsenate.} \end{array}\right.$$

These salts remind us in formula of Na_3AsO_3, sodium arsenite, and Na_3AsO_4, sodium arsenate. The difference is merely in the presence of sulfur in place of oxygen. The name thio- is then prefixed to the usual name.

When these solutions of soluble thio-salts are acidified we might expect to get, at least in equilibrium, the free thio-acids from which the salts were derived. But precipitates of the sulfides are obtained. The explanation is simple. The thio-acids are indeed liberated, but decompose at once with loss of hydrogen sulfide (much like spontaneous loss of water from —OH groups in oxygen acids) and the simple insoluble sulfides are left.

It is important to note that warming arsenic trisulfide with plain sodium sulfide (Na_2S) does not change the valence of the arsenic, does not oxidize it. But warming with sodium polysulfide (Na_2S_2) gives us a thio-salt (Na_3AsS_4) in which the arsenic has a valence of five, and on decomposing this compound with an acid arsenic pentasulfide results. The extra sulfur in the sodium polysulfide simply added on to the arsenic, giving it the full valence of five. These reactions are of the utmost importance in qualitative analysis.

Antimony

History.—Antimony, or perhaps its sulfide, was used as a medicine or cosmetic in the Orient before the Christian era. Basil Valentine, a German monk of the fourteenth century, wrote fully and most reverently of the wonders of antimony. His book, *The Triumphal Chariot of Antimony*, preserved much chemical information. By the close of the eighteenth century the chemistry of antimony was much better known than that of any other element.

Occurrence.—Although found free in small quantities, the element is found chiefly as the sulfide (Sb_2S_3). China practically supplies the world's annual need of 23,000 tons.

Preparation.—The sulfide " stibnite " is often reduced by roasting with scrap iron:

$$Sb_2S_3 + 3\ Fe \longrightarrow 3\ FeS + 2\ Sb.$$

By another method the sulfide is melted away from the gangue or common rock in the ore and is then roasted into the oxide and reduced by hot carbon.

Properties.—The change from the non-metallic nature of nitrogen and phosphorus is noticeable in arsenic, but with antimony it becomes decided. This element reacts with sulfuric and nitric acids to form sulfates and nitrates of antimony. Here the element plays the part of a metal. Yet it is unlike the metals in that it is a poor conductor of heat and electricity and its hydroxides are acidic, forming salts with bases.

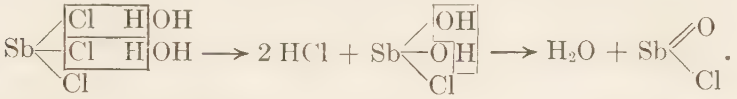
Antimony is a silver-white, brittle element, melting at 680°, and boiling at 1440°. Its specific gravity is 6.7. It expands slightly on cooling from the liquid to the solid state. Only the oxidizing acids attack it and these may form insoluble oxides. In qualitative analysis it is convenient to remember that antimony and tin are the only metals converted into such insoluble oxides by concentrated nitric acid. Antimony reacts readily with phosphorus, arsenic, sulfur and the halogens.

Uses.—Its chief value is in making alloys, such as type metal, lead-antimony grids from storage batteries, bearing metals, and others. Its property of expanding on cooling makes it essential to type metal, for a sharp imprint of the type is desired.

Oxides.—The oxides expected from its similarity to phosphorus occur. Antimony trioxide (Sb_2O_3) is more basic than acidic, but the pentoxide is decidedly acidic. The latter loses oxygen if strongly heated and drops to the lower oxide. A third oxide (Sb_2O_4) is not of much interest.

Salts.—Antimony nitrate ($Sb(NO_3)_3$) as well as the sulfate ($Sb_2(SO_4)_3$) is almost completely hydrolyzed, which shows that the hydroxide of antimony is a very weak base. (See Hydrolysis, page 223.) When the trioxide is boiled with potassium hydrogen tartrate ($KHC_4H_4O_6$) tartar emetic is formed. Its formula, $K(SbO)C_4H_4O_6$, shows that one hydrogen of the acid salt is replaced by the antimonyl group (SbO—). Other salts where this group acts like a metal are known. This particular salt is used in medicine and as a mordant in making certain fabrics takes up dyes. Antimony trichloride ($SbCl_3$), or "butter of antimony," is used to give the dull finish to gun barrels.

The trichloride is hydrolyzed to the basic chloride, which then loses water, forming the insoluble oxychloride:



On boiling the chloride is completely hydrolyzed to $Sb(OH)_3$, which loses water and becomes Sb_2O_3.

Exercise 9.—How could you change from KH_2SbO_4 to potassium metantimonate?

Stibine.—Antimony compounds are reduced by active hydrogen with formation of the poisonous gas stibine just as arsine is formed. In fact the famous Marsh test for arsenic can be applied to antimony. The antimony spot is blacker than the arsenic spot and is not dissolved by a solution of sodium hypochlorite (unlike arsenic). Arsine reacts with a solution of silver nitrate with formation of black, finely divided silver, but stibine reacts to form silver antimonide ($SbAg_3$). Stibine is best made by the action of dilute hydrochloric acid on an alloy of antimony and magnesium in the absence of air.

Sulfides and Thio-Salts.—Freshly precipitated antimony trisulfide is orange-red, but when melted it is black like the mineral stibnite:

$$2\,SbCl_3 + 3\,H_2S \longrightarrow 6\,HCl + Sb_2S_3.$$

It dissolves in alkaline sulfides like arsenic sulfide. Instead of thioarsenic acid we refer to thioantimonic acid, etc. The oxidation relations are the same and spontaneous decomposition of the thioacids with precipitation of simple sulfides follows the same rules. Write all the formulas and reactions that are given under thiocompounds of arsenic with the substitution of Sb for As and they will be correct.

BISMUTH

Bismuth has been known for centuries, although for some time confused with antimony. The characteristic properties were discovered by Pott in 1739.

Occurrence.—Bismuth is much scarcer than the other members of the group. The free element is found as well as the sulfide (Bi_2S_3), oxide (Bi_2O_3), and the telluride (Bi_2Te_3). Bismuth is now obtained chiefly from anode slimes in the electrolytic refining of copper, lead and tin. The world uses only 270 tons and most of this comes from Bolivia.

Preparation.—Roasting the sulfide ore and then reducing the oxides with hot carbon is a common method of preparation.

Properties.—Bismuth is strictly metallic. It is silver-white with a reddish tint, brittle, and crystalline. It melts at 269°, boils at 1435° and, although stable in air, burns to the trioxide (Bi_2O_3). It unites directly with the halogens and decomposes steam at a red heat.

There is no use for the element alone but in alloys it is rather important. This will be discussed in the chapter on Alloys.

Compounds.—Bismuth trioxide, Bi_2O_3, is basic, but the other oxides, BiO, Bi_2O_4, and Bi_2O_5, are neither basic nor acidic. The trichloride formed by treating bismuth with chlorine or aqua regia hydrolyzes with precipitation of $BiOCl$. (See the similar compound of antimony.) The nitrate ($Bi(NO_3)_3$) is hydrolyzed very noticeably, producing a salt used in medicine under the name "bismuth subnitrate." X-ray pictures of the intestines are made possible by doses of this salt. Sulfur compounds in the intestine change this into the sulfide, which is impermeable to the X-rays and hence appears black on the photograph. However, barium sulfate is displacing bismuth compounds for this purpose.

Probably only salts of trivalent bismuth are known. There is a compound similar to arsine. The element is too metallic for its sulfide to dissolve in alkaline sulfides.

EXERCISES

10. Suppose you knew that the chloride of bismuth was 66 per cent bismuth and 34 per cent chlorine and that the specific heat of bismuth was 0.0303. How would you calculate the atomic weight of bismuth and the correct formula for the chloride? You are supposed to know that the atomic (and equivalent) weight of chlorine is 35.46.

11. A certain copper ore contained 1 per cent of arsenic. What weight of arsenious oxide could be formed from 100 tons of ore?

12. What volume of phosphine at 30° and 765 mm. will be obtained by the action of an excess of water on 20 g. of calcium phosphide?

13. How many g. of phosphorus can be made by the electrothermal process from a ton of calcium phosphate (70 per cent pure)?

14. What is the molecular formula of arsenic if a liter of its vapor, recalculated to standard conditions, weighs 13.7 g.?

15. What is the "thermal process" of making phosphoric acid? How may this new development influence agriculture?

16. What is the leading demand for arsenic?

17. Calculate the percentage of P_2O_5 in "superphosphate," $Ca(HPO_4)_2$.

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"Insecticides," *Chemical Industry,* 368T, Sept. 1927.

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"Matches," *J. Chem. Ed.,* *6*, 1359, (1929).

N NH_3 [illegible]
P PH_3
As
Sb
Bi (metallic)

CHAPTER XXIX

THE HYDROCARBONS. FUELS

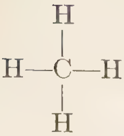
Homologous Series.—There are several hundred hydrocarbons (compounds of hydrogen and carbon), most of them found in petroleum, natural gas, asphalt, and coal tar products. These are divided into a few series, with some very definite relationships between the members. Rubber is a hydrocarbon, $(C_5H_8)x$.

METHANE SERIES C_nH_{2n+2}		ETHYLENE SERIES C_nH_{2n}		ACETYLENE SERIES C_nH_{2n-2}		BENZENE SERIES C_nH_{2n-6}	
Methane	CH_4			(Ethine or)			
Ethane	C_2H_6	Ethylene	C_2H_4	Acetylene	C_2H_2		
Propane	C_3H_8	Propylene	C_3H_6	Propine	C_3H_4		
Butane	C_4H_{10}	Butylene	C_4H_8	Butine	C_4H_6		
Pentane	C_5H_{12}	Pentylene	C_5H_{10}	Pentine	C_5H_8		
Hexane	C_6H_{14}	Hexylene	C_6H_{12}	Hexine	C_6H_{10}	C_6H_6	Benzene
Heptane	C_7H_{16}	Heptalene	C_7H_{14}	Heptine	C_7H_{12}	C_7H_8	Toluene
Octane, etc.	C_8H_{18}	Octalene	C_8H_{16}	Octine	C_8H_{14}	C_8H_{10}	Xylene

In each series any one member differs from its neighbor by one carbon and two hydrogens (CH_2). This regular progression in molecular weight is the reason for the name, "homologous series." The general formula for the series is useful. For example, in the methane series (so called from the name of its simplest member) we know that a hydrocarbon with five carbons must have twelve hydrogens in the molecule (C_5H_{12}) because in the series formula (C_nH_{2n+2}), the n is 5 in this case and $2n + 2 = 12$.

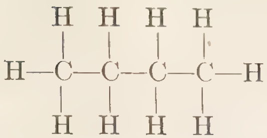
The methane and benzene series are by far the most important. The entire methane series up to a molecule of 60 carbon atoms is found in petroleum. The first member CH_4 makes up over 90 per cent of natural gas. The first four members are gases at ordinary temperatures: from C_5H_{12} to $C_{15}H_{32}$ they are liquids and from $C_{16}H_{34}$ up they are solids.

The existence of so many compounds of two elements depends wholly on the tetravalence of carbon and the ability of carbon atoms to hold other carbon atoms in long chains or rings.



$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ & H & \end{array}$$

and



$$\begin{array}{cccccc} & H & H & H & H & \\ & | & | & | & | & \\ H- & C- & C- & C- & C & -H \\ & | & | & | & | & \\ & H & H & H & H & \end{array}$$

illustrate this. Name them.

Methane.—Methane is formed when many kinds of organic matter are heated out of contact with air. Thus the gases from the distillation of coal and wood contain it. Inflammable bubbles may be stirred up from marshy pools where decaying vegetation has formed methane or "marsh gas." It is often found in coal mines, where it is known as "fire damp," and is thus the cause of dangerous explosions. Petroleum contains some of this substance but the chief source is natural gas, which may contain 90 to 95 per cent of methane.

Priests of the ancient Parsee fire worshippers attended "eternal fires" 2,500 years ago, fires that we now know were burning jets of natural gas escaping from rock fissures in the oil district around Baku, Russia. Only recently did the last of the priests depart. George Washington wrote in 1775 of a burning natural gas jet in West Virginia.

It was not until 1872, however, that a gas well was drilled and the supply piped five miles to Titusville, Pennsylvania. The industry is now so enormous that 1,000 billion cubic feet are consumed annually in the United States. It is an ideal domestic fuel, yet three-fourths of it is used in industry. (How is "carbon black" made?)

It is a colorless, odorless gas, inflammable, insoluble in water and is rather indifferent chemically.

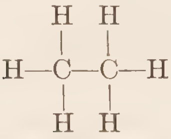
Natural gas is a valuable fuel, yielding carbon dioxide and water on combustion. When 1000 cubic feet of the gas burns, over 10 gallons of water could be collected by chilling the vapors. Natural gas and oil occur in the same fields and, in fact, the gas is really the volatile part of the oil deposit. The great gas fields of Pennsylvania, West Virginia, Ohio, and Indiana have wasted most of their resources and thus a great national asset will soon be exhausted. Louisiana, Oklahoma, Texas, and West Virginia now lead. It is the pressure of reservoirs of this gas that forces oil out in "gushers."

Much "high-test" gasoline 1,660,000,000 gallons yearly, has been extracted from natural gas by dissolving the gasoline vapor in heavy oils or by adsorbing in porous carbon or by compression methods. This very volatile "casing-head" gasoline is blended with heavier gasolines to make a good motor fuel.

It is possible to make many valuable derivatives from methane, as will be shown in the next chapter.

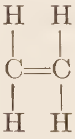
Exercise 1.—How many grams of oxygen are required to burn 100 liters of methane, both gases being measured under standard conditions?

Ethylene, C_2H_4.—This colorless, inflammable gas burns with a luminous flame due to the separation of much incandescent carbon. To its presence (2 per cent in coal gas) is due much of the illuminating power of some commercial gases. It is the first member of a series of unsaturated hydrocarbons. In methane, carbon has its full valence of four, but in ethylene, C_2H_4, the two carbons use only a valence of three each. In the structural formula this unsaturated condition may be represented by a double linkage between the carbons. This means only the kind of unsaturation existing in ethylene.



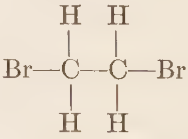
$$\mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}H}$$

Ethane (Saturated)



$$\mathrm{\underset{H}{\overset{H}{C}}{=}\underset{H}{\overset{H}{C}}}$$

Ethylene
(Unsaturated)



$$\mathrm{Br{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}Br}$$

Ethylene Bromide
(Saturated)

As a result of its unsaturation, this compound has an ability to add on bromine and other elements until the usual valence of four is exercised by the carbon. A common laboratory experiment is to pass ethylene gas into bromine, securing the heavy, colorless liquid, ethylene bromide, $C_2H_4Br_2$. Ethylene itself may be made from alcohol by heating with concentrated sulfuric acid. The effect of the reaction is removal of the elements of water from ethyl alcohol:

$$C_2H_5OH \longrightarrow H_2O + C_2H_4.$$

Passage of ethyl alcohol vapors over heated Al_2O_3 or ThO_2 produces the same result. When any saturated hydrocarbon is heated strongly in absence of air some ethylene is produced. Even methane can be made to yield it:

$$2\,CH_4 \longrightarrow 2\,H_2 + C_2H_4.$$

Ethylene is largely used for blow torch welding and cutting, comparing favorably with acetylene for this purpose. Ethylene is the starting point in the manufacture of ethylene dichloride which promises to be of great service in shortening the period of dormancy of seed potatoes and some flowering plants. Propylene C_3H_6, the second member of the ethylene series has similar properties.

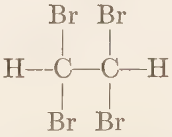
Ethylene is of great value as an anæsthetic. Citrus fruits turn yellow more rapidly under its influence. In the use of tetra-ethyl lead as an "anti-knock" compound to be added to gasoline continues, ethylene bromide, $C_2H_4Br_2$, will have a large sale, for its use in connection with tetra-ethyl lead is considered desirable (p. 173). Ethylene is fundamental in modern warfare for it reacts readily with sulfur monochloride to form mustard gas.

$$2\,C_2H_4 + S_2Cl_2 \longrightarrow (C_2H_4Cl)_2S + S.$$

Acetylene, C_2H_2.—This gas has a lower percentage of hydrogen than ethylene, so it is still more unsaturated. Each carbon is able to add on two bromine atoms or other atoms and become saturated with the usual four valences. The structural formula represents the linkage between the carbons by three bonds, but this is only to be counted as representing the particular degree of unsaturation existing in acetylene:

$$H—C \equiv C—H$$

Acetylene
(Unsaturated)



$$\begin{array}{ccccccc} & & Br & & Br & & \\ & & | & & | & & \\ H & — & C & — & C & — & H \\ & & | & & | & & \\ & & Br & & Br & & \end{array}$$

Acetylene Bromide
(Saturated)

The formation of the gas by addition of water to calcium carbide has been given previously ($CaC_2 + 2\,H_2O \longrightarrow Ca(OH)_2 + C_2H_2$). A very little is formed in the carbon arc when hydrogen is present. When ethylene is passed through very hot tubes some acetylene is formed:

$$C_2H_4 \longrightarrow C_2H_2 + H_2.$$

Acetylene fed with oxygen in the acetylene torch produces an intensely hot flame. With this a 6-inch steel shaft can be cut through in less than a minute and heavy plates cut with equal speed. The formation of acetylene is endothermic, that is, 53,880 cal. are absorbed when a gram molecular weight is prepared. Consequently when acetylene is burned the total heat given off is the sum of the heat of combustion of the elements carbon and hydrogen plus this 53,880 cal. liberated when acetylene is decomposed.

Petroleum.—Petroleum, varying in color from a light greenish-yellow to a green or reddish-brown, is a mixture of hydrocarbons, although some derivatives containing oxygen, nitrogen, or sulfur may be present. It is sometimes limpid but usually rather thick.

The origin of petroleum is still in dispute. Probably it was derived from animal and vegetable matter buried under layers of sediment but the action of water on metallic carbides deep in the earth has been suggested as one of the earlier theories.

The composition of petroleum from different fields varies considerably. Eastern United States produces oil largely made up of the methane (paraffin) series, while California produces oil containing much asphaltic material and naphthenes (peculiar type of ring compounds of the general formula C_nH_{2n}). Borneo-Java oil is rich in benzene and its homologues. Mexican crude oil is, unfortunately, rich in sulfur compounds. In petroleum from most fields the cyclic hydrocarbons of the general formula C_nH_{2n-x} are important constituents.

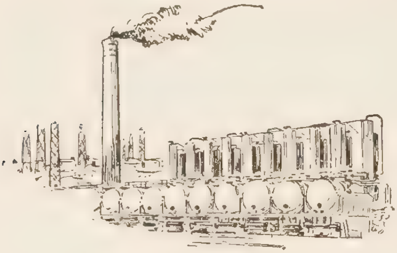


Fig. 108.—A bank of petroleum stills.

The United States produces almost three-fourths of the world's petroleum, with Venezuela second, Russia third, and Mexico fourth. Lesser but important deposits are found in Mesopotamia, the Dutch East Indies, Colombia, Peru, Egypt, Roumania, Poland, India, Japan, Persia, and Argentina. Herodotus writes of this oil as known to the Persians in 450 B.C., but there was no particular use for it until it occurred to Colonel Drake in 1859 to drill a well near Oil City, Pennsylvania. The average depth of wells is 3000 feet, but a few are a mile and a half in depth. Some of the Russian "gushers" have yielded 200,000 barrels a day while the gas pressure was high. The Pennsylvania field has now declined to a small percentage of our national production and the leadership has been taken by Texas, California, Oklahoma, Louisiana, Kansas, Arkansas, and Wyoming. Kansas and

Oklahoma send much of their oil over a thousand miles through 6-inch pipes to refineries near New York City. The total production of the United States in 1928 was 900,000,000 barrels of 42 gallons each.

WORLD PETROLEUM PRODUCTION

	Per Cent of Total	1928, Barrels
United States	68.2	902,000,000
Venezuela	8.	106,000,000
Russia	6.7	87,800,000
Mexico	3.8	50,150,000
Persia	3.2	42,000.000
Roumania	2.3	30,000,000
Dutch East Indies	2.2	28,500,000
Colombia	1.5	20,000,000
Peru	0.9	12,000,000
Argentina	0.7	9,000,000
India	0.6	8,000,000
Trinidad	0.6	7,750,000
Poland	0.4	5,500,000
Sarawak	0.4	5,300,000
Japan	0.1	1,800,000
Egypt	0.1	1,800,000
Ecuador	0.1	1,100,000
Miscellaneous	—	3,300,000
Total		1,322,000,000

The average well costs $22,540 making the 1928 total spent in the United States, drilling oil and gas wells, fully $500,000,000.

Refining crude petroleum is essentially the separation by distillation of the more volatile from the less volatile constituents. The crude oil is heated by direct flame in huge steel cylinders. although tube stills are coming into prominence. At first, the very volatile fractions including gasoline come off and are separated for further treatment. As the temperature rises the kerosene fractions (still higher boiling point) come off and later the heavier lubricating oils. A current of superheated steam is forced through the boiling oil at this point to assist in distilling over the lubricating fractions. The various fractions are distilled again, some of them with steam, and finally the liquids listed below are secured. The other distillates are mixtures of two or more hydrocarbons. the term *benzine* is used rather loosely but should not be applied to the benzene from coal tar. A list of the fractions follows:

NAME	COMPONENTS	BOILING POINT	USES
Petroleum ether	Pentane-hexane	40°–90°	Solvent
Gasoline	Hexane-nonane	90°–210°	Motor fuel, solvent
Kerosene	Decane-hexadecane	210°–300°	Illuminating oil
Middle fractions (gas oil)	About 40% of the crude oil	225°–375°	To "crack" into more gasoline or to enrich water gas; domestic furnace fuel
Lubricating oils		about 350°	Lubrication
Vaseline			Candles, sealing jellies, waterproofing
Paraffin			
Tar residue			Artificial asphalt
Petroleum coke 1,000,000 tons, yearly			Domestic fuel, electrodes

Methane, propane, butane, and pentane can be isolated as pure compounds. The light naphthas (70°–100°) are much used as solvents for rubber and varnishes.

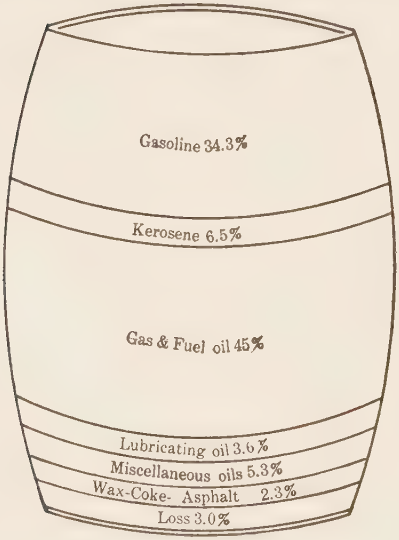


FIG. 109.

Paraffin (645,000,000 pounds annually) is not a solid residue left after everything else has been distilled off, but is crystallized from the lubricating fractions by chilling. Vaseline or petrolatum is prepared from the heavy distillates. Our annual production of asphaltic tars from oil refining is 4,000,000 tons.

Light naphthas (70° C.–100° C.) much used as solvents for rubber and varnishes and as airplane fuels, are generally mixed with heavy naphthas (100°–150°), also used as solvents, and with "benzine" dry-cleaning fluids, to form commercial gasoline.

The losses in the oil industry are still too great. Several times as much oil is left in "exhausted" sands as is pumped out. The evaporation losses in storage tanks total one billion gallons annually in this country alone, although this loss is being checked by breathing bags and floating roofs and heat-reflecting paints such as zinc oxide and aluminum. The problem of removing water persistantly emulsified in the crude oils of California, Mexico, and some other fields has not yet been fully solved. Fully 200,000,000 barrels of crude oils with a serious water content are produced in the world annually. To complete this dismal picture of losses we may add that only 5 per cent of the gasoline burned is effective in moving the car. This, however, is a problem for the automotive engineer, not for the chemist.

In 1906 the American petroleum industry existed primarily to supply the world with 33,000,000 barrels of kerosene principally for use in kerosene lamps, but by 1928 this petroelum industry had come to exist primarily to supply 377,000,000 barrels of gasoline, 56,000,000 barrels of kerosene, and also the vitally important lubricating oils. This change was forced by automobiles, 25,000,000 in this country and 32,000,000 in the whole world.

The "cracking" of the middle fractions is a very recent development of tremendous importance. This distillate had little use previous to 1913, when Burton discovered that oils heated to 375° C. at one hundred pounds pressure yielded gasoline where there was none before. The hydrocarbons decompose and some of the new combinations are in the form of gasoline molecules. To be exact, this general principle was known earlier, but Burton applied it successfully, and his process was, for several years, the principal one operating on a large scale.

Burton's discovery (1913) came just in time to help save the Allies in the Great War. This was so much a war of auto transportation of men and supplies to the front lines that there was never enough gasoline motor fuel for the pressing military needs. But here was a creation of new gasoline in great quantity in addition to the amount naturally occurring in the petroleum. Before protesting about the price of gasoline, motorists may reflect that but for the large-scale development of the cracking process, prices would be still higher and there would not be enough gasoline to supply the demand.

The average "straight run" gasoline content of crude petroleum is about 20 per cent, so straight distillation supplies only one half of the 15,800,000,000 gallons of gasoline this country made in 1928. One-tenth of this great volume of fuel is "casing-head" gasoline separated from natural gas and one third is cracked gasoline. The cracked product is rapidly increasing in amount.

Cracking, already familiar in the thermal decomposition of $H_2S \longrightarrow H_2 + S$, may be approximately represented for petroleum hydrocarbons by the following equations:

$$\begin{array}{ccccc} C_{12}H_{26} & \longrightarrow & C_6H_{14} & + \; C_5H_{12} & + \; C, \\ \text{b.pt. } 216^\circ & & \text{b.pt. } 69^\circ & \text{b.pt. } 36^\circ & \\ C_{12}H_{26} & \longrightarrow & C_7H_{16} & + \quad C_5H_{10}. & \\ & & \text{b.pt. } 98^\circ & \text{b.pt. } 38^\circ. & \end{array}$$

The ***Burton cracking process*** dominated the situation for several years but is now being displaced by improved processes such as the ***Dubbs, Cross, Holmes-Manley*** and others. The deposition of carbon and its removal was serious with Burton stills. The Holmes-Manley still incloses in a furnace a set of four vertical tubes, 5 feet in diameter and 40 feet high, arranged so the oil circulates. By means of a scraper the carbon liberated is drawn off at the bottom of the tubes.

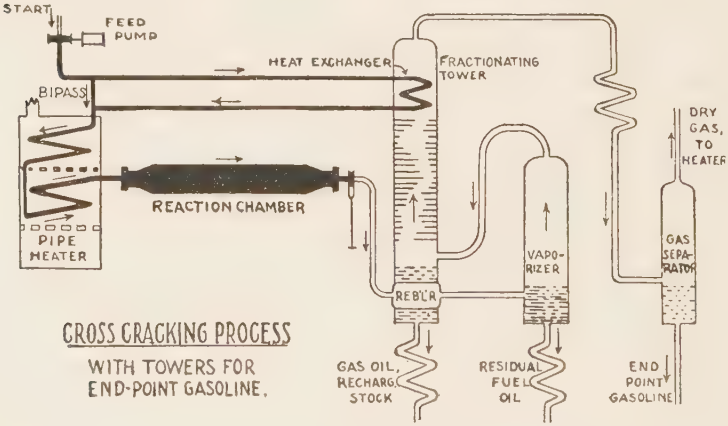

START
FEED PUMP
HEAT EXCHANGER
FRACTIONATING TOWER
BIPASS
DRY GAS, TO HEATER
REACTION CHAMBER
PIPE HEATER
VAPO-RIZER
GAS SEPA-RATOR
REB'L'R
CROSS CRACKING PROCESS
WITH TOWERS FOR END-POINT GASOLINE.
GAS OIL, RECHARG. STOCK
RESIDUAL FUEL OIL
END POINT GASOLINE

FIG. 110.

By the ***Cross cracking process*** the gas oil is preheated in a 500 foot coil of 3-inch pipe placed in the top of a fractionating tower and in the top of a furnace. Then the oil is further heated to 500° at 600–700 pounds pressure in a 4000-foot coil of pipe set in a lower and hotter part of the furnace. Next the oil is forced to a horizontal cast steel "reaction chamber" (40 feet long and 4 feet wide) where it reacts for 15 minutes. From this digestor it passes a pressure relief valve, expanding into a vaporizing tower. About 90 per cent vaporizes (because of the high temperature and reduced pressure) and the residue is discharged from the bottom. The vapor passes to the fractionating tower where the higher-boiling portion is condensed and the gasoline continues on as vapor to the condenser where it is collected as liquid. If the residual stock is run through again the yield of gasoline from fresh gas oil may be nearly doubled.

The modern cracking process which parallels this "growing of two blades of grass where but one grew before" is one of the greatest triumphs of the engineering mind; and its efficiency will be increased.

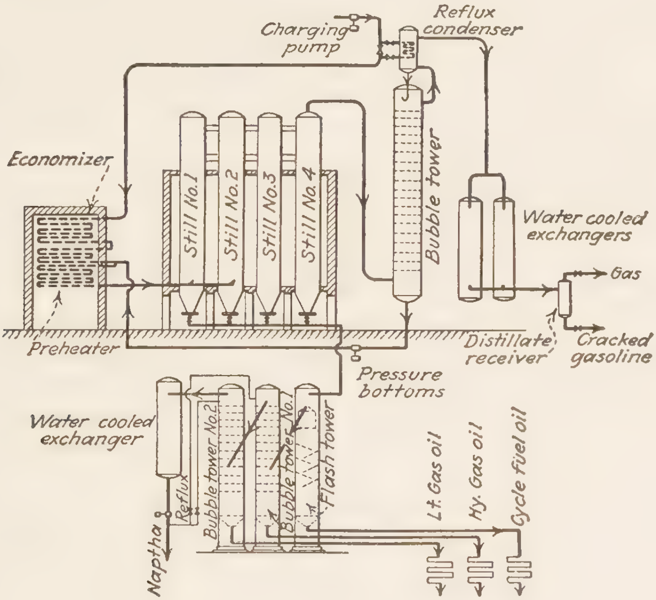

Charging pump
Reflux condenser
Economizer
Still No.1
Still No.2
Still No.3
Still No.4
Bubble tower
Water cooled exchangers
Gas
Preheater
Distillate receiver
Cracked gasoline
Pressure bottoms
Water cooled exchanger
Reflux
Bubble tower No.2
Bubble tower No.1
Flash tower
Naptha
Lt. Gas oil
Hy. Gas oil
Cycle fuel oil

FIG. 111.—The Holmes-Manley cracking still.

The use of anhydrous aluminium chloride as a cracking agent operating at ordinary atmospheric pressure is growing.

It has already been demonstrated that the tars obtained by the distillation of wood may be cracked to yield excellent anti-knock motor fuel, tar acids or phenols useful as antiseptics and disinfectants, and fuel gas.

It is possible to hydrogenate petroleum with the aid of a catalyst under high pressure and proper temperature so as to increase the yield of gasoline. This is just the opposite of cracking and is analogous to the hydrogenation of fats and of coal.

The Diesel engine, exploding in the cylinder a charge of heavy fuel oil, makes a different demand on the refining process as does the household oil burner also operating on fuel oil. In the last five years this country multiplied by ten its installation of such oil-fired household furnaces.

The threatened exhaustion of oil deposits in the not very distant future was once alarming from the standpoint of lubrication. Modern machinery makes enormous demands on special oils for the different lubrication needs. Control of the world's great oil fields is a prize that nations will strive for. Steamships and battle cruisers are finding crude oil or waste refinery fractions an ideal fuel. The liquid fuel is atomized by air or steam and burned under boilers as a spray. The gain in speed, cruising radius, and saving in labor is vital.

Oil Shale.—When our petroleum deposits are exhausted we can, if necessary, develop the enormous deposits of oil shale found in Colorado, Utah, Montana, Nevada, California, and Indiana. These are sufficient to last for centuries. Under present competition with oil deposits it is unlikely that the shale industry will soon be developed to any great extent, but in time this may change. The oil does not occur in the shale as such, but is obtained by retort distillation which breaks down complex organic compounds in the shale. Among the distillation products are oils, ammonia, and fuel gas.

The Colorado shale, easily mined, covers an area of 1500 square miles with a possible yield of 24,000,000 barrels of oil to the square mile. This area could furnish 300,000,000 tons of ammonium sulfate—a boon to the farmer. One barrel of oil can be distilled from one ton of shale.

Asphalt was, doubtless formed by further chemical changes in petroleum. A great lake of it occurs in the island of Trinidad and small deposits in several of our states. Its use in surfacing streets is well known.

Alcohol added to gasoline gives an improved fuel and absolute alcohol in tonnage lots is now produced for that purpose. Ordinary 95 per cent ethyl alcohol does not mix with gasoline. Dehydration by distillation over lime had been used but the newest method of making absolute alcohol applies some interesting principles of distillation.

The vapor pressure of alcohol is reduced in the presence of a third substance such as benzene which mixes thoroughly with alcohol but not with water, while the vapor pressure of the water remains unchanged. While a mixture of 96 per cent alcohol with 4 per cent water distils unchanged, the vapors from this mixture plus benzene contain more water than the residual liquid and finally only absolute alcohol is left. (Compare p. 61.)

Benzene and Its Series, C_6H_6.—Benzene was discovered in 1825 by Faraday, and about twenty years later was found by A. W. Hofmann in the gases distilled from coal tar. It is a colorless liquid, lighter than water and insoluble in water, of a slight odor (not unpleasant), melting at 6°, boiling at 80.4°. It burns with a smoky flame and is an excellent solvent for grease, resins, and rubber. It has long been used in paint and varnish removers and in the manufacture of artificial leather.

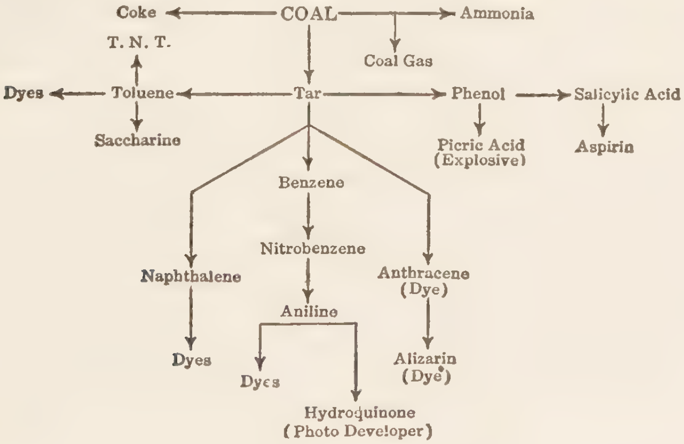

Coke
COAL
Ammonia
T. N. T.
Coal Gas
Dyes
Toluene
Tar
Phenol
Salicylic Acid
Saccharine
Picric Acid (Explosive)
Aspirin
Benzene
Nitrobenzene
Naphthalene
Anthracene (Dye)
Aniline
Dyes
Dyes
Alizarin (Dye)
Hydroquinone (Photo Developer)

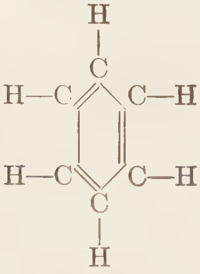
Fig. 112.—Coal derivatives.

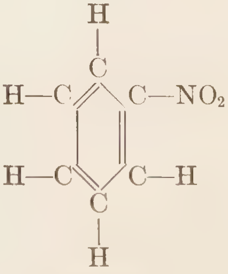
Chemically benzene must be classed as an unsaturated hydrocarbon, since it is capable of adding on six hydrogen atoms or six bromine atoms per molecule. It reacts with nitric acid to form nitrobenzene, $C_6H_5NO_2$. and this in turn is reduced by active hydrogen to aniline, $C_6H_5NH_2$, the mother substance of a host of beautiful "aniline dyes." It can also be attacked by hot concentrated sulfuric acid and other reagents. In fact over one-half of all carbon compounds are derivatives of benzene:

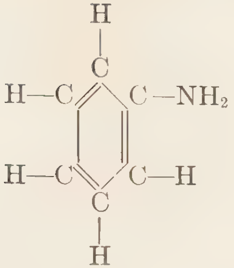
$$C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O,$$
$$C_6H_5NO_2 + 3\ H_2 \longrightarrow C_6H_5NH_2 + 2\ H_2O.$$

A very interesting line of evidence shows us that the six atoms of benzene are tied together in a ring, very different from the chains of carbons in the methane series. A comparison of a few structural formulas of benzene and its derivatives will be worth while.

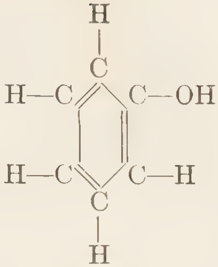
It is sometimes carelessly stated that benzene (with toluene) is obtained by distilling coal tar, itself produced by distillation of coal. But the fact is that very little benzene and toluene are distilled from the tar. The gases from the coal retorts are scrubbed by a spray of some heavy oil which dissolves benzene and toluene. From this solution they are later removed by distillation. During the World War the demand for benzene as a source of the high explosive, picric acid, was great and only exceeded by the demand for toluene as a source of T. N. T. (trinitrotoluene). Naturally the prices soared, and the by-product coke oven industry grew by leaps and bounds. But even in peace times great quantities of benzene will be in demand, if not as the starting point in making dyes, drugs, and photographic chemicals, then as a motor fuel. By a slight adjustment of the carburetor, benzene (or benzol as the public insists on calling it) yields more power in the engine than does gasoline. Already it is in very extensive and rapidly growing use for this purpose. The United States could produce perhaps 200,000,000 gallons a year without increase in the tonnage of coke, but even this much would not be enough. Our 25,000,000 motors now use 15,800,000,000 gallons of gasoline a year.


Benzene

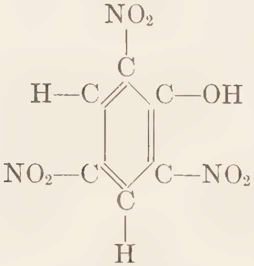

Nitrobenzene



Aniline



Phenol
(Carbolic Acid)



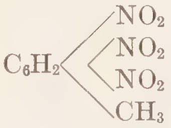
Trinitrophenol
(Picric Acid)

Toluene, C_7H_8.—This colorless liquid, boiling at 110°, is closely associated with benzene in manufacture from bituminous coal and closely resembles benzene in many properties. Its special interest to the public is as the source of the world's greatest explosive, "T. N. T." (trinitrotoluene). Toluene differs from benzene by having a methyl group ($—CH_3$) in place of one hydrogen atom. On treatment with concentrated nitric acid and sulfuric acid three nitro groups ($—NO_2$) are introduced in place of three more ring hydrogen atoms:

$$C_6H_5 \cdot CH_3 + 3\ HNO_3 \longrightarrow 3\ H_2O + C_6H_2(CH_3)(NO_2)_3.$$

C_6H_6
Benzene

$C_6H_5 \cdot CH_3$
Toluene



$$C_6H_2 \left\langle \begin{matrix} NO_2 \\ NO_2 \\ NO_2 \\ CH_3 \end{matrix} \right.$$

T. N. T.

Coal Tar.—The distillation of bituminous coal has often been mentioned in this text, especially in connection with ammonia and benzene. Until recent years coke was produced in "beehive" ovens without capturing any of the gaseous products. But war prices of ammonia, benzene, toluene, phenol, and the dyes led to a very rapid expansion of the by-product coke oven industry. The most modern ovens consist of banks of narrow brick chambers each about 40 feet long, 10 feet high, and 1.5 feet wide. Each chamber holds 12–18 tons of bituminous coal. The ovens are separated by a series of vertical flues in which gas is burned to furnish the heat for coking. The newest ovens coke the charge in 15 hours.

The volatile products are washed with water to catch ammonia and some tar and with heavy oil to catch most of the benzene and toluene. The ammonia is first absorbed in wash water from which it is afterwards driven off by addition of lime and passage of steam through the liquor. The tar is condensed and the remaining coal gas finally purified for use as a fuel. Coal tar is a black, disagreeable mass, but from it are made the most delicate colors the world ever saw and some of the most beneficial medicines as well as dainty perfumes. The blackness is due to free carbon. This tar was once used only for making roofing paper or felt and has been burned as a fuel, but now the demand for its fractions is large. On redistilling the tar the following products, given in order of volatility are obtained:

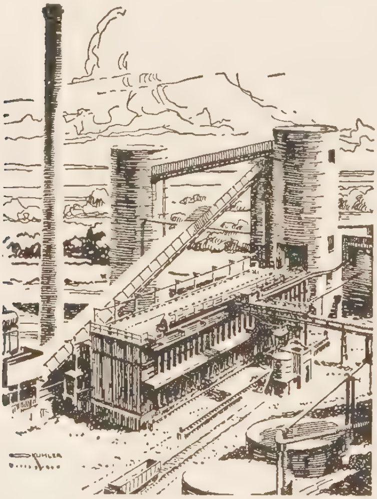


FIG. 113.—A bank of by-product coke ovens.

1. Light oil containing a small part of the benzene and toluene.
2. Middle oil containing phenol (carbolic acid).
3. Heavy oil containing creosote.
4. Anthracene oil.
5. Residue of pitch.

The middle oil yields carbolic acid used as a disinfectant and as a source of the explosive, picric acid. Naphthalene (moth ball material) is also taken from this fraction. It was used as the starting point in making artificial indigo.

The heavy oil or creosote is in great demand as a wood preservative. Each year 275,000,000 gallons are used, and yet fewer than one-third of the railroad ties of this country are creosote dipped. From the anthracene of the next fraction is made alizarin, a most important dye, once obtained only from the madder plant. The pitch left in the still has extensive use in the manufacture of roofing paper, surfacing of roads, filling between the blocks in paving, and in coating iron pipes. If heated long enough, hard pitch results, and this may be used as a pulverized fuel low in ash and sulfur.

More than ninety per cent of our production of coke is now made in by-product ovens, while in 1913 only 27 per cent was so made. Our by-product ammonia in 1929 was equivalent to about 890,000 tons of ammonium sulfate.

Low-Temperature Carbonization of Coal.—The usual high-temperature coke oven operates at about 900°–1200° C. A new process of coking at 500°–700° C. is now being tested commercially with promising results. The semi-coke formed under these conditions is a far better domestic fuel than ordinary coke or than soft coal. It is smokeless, ignites easily, and has greater radiant efficiency than coal or high-temperature coke. This "coalite" contains from seven to fifteen per cent volatile matter while common coke contains only one or two per cent.

This tar oil is more like petroleum and may be cracked to yield 22 per cent of motor fuel of high anti-knock value. The only increased return is the 15 gallons extra tar oil secured by the best low-temperature coking process. After all, the economic success of the project must depend largely upon the willingness of the public to pay enough for the excellent, smokeless, semi-coke as a domestic fuel. Some of the experimental plants now operating are designed to use this semi-coke for a powdered industrial fuel or in gas making.

Parr's process of preheating the coal to 300° C. to remove water and carbon dioxide, followed by relatively quick coking at 750° C.–800° C. produces a real coke, not a semi-coke, from Illinois coal which is said to be non-coking. Yet this new coke with 5 per cent volatile matter is easy to ignite.

APPROXIMATE COMPARATIVE YIELDS OF HIGH AND LOW TEMPERATURE CARBONIZATION PROCESSES
(*A. C. Fieldner*)

		HIGH-TEMPERATURE CARBONIZATION BY-PRODUCT COKE OVEN	LOW-TEMPERATURE CARBONIZATION	
			Externally Heated Retort	Internally Heated Retort
Coke	per cent	60–70	70–80	60–75
Volatile matter in coke	per cent	1–2	7–15	7–15
Gas	cu.ft./ton	11,000–12,000	3,000–5,000	20,000–50,000
Calorific value of gas	B.t.u./cu.ft.	520–580	800–1,000	150–250
Tar	gal.	10–12	20–30	18–20
Specific gravity of tar		1.19	1.07–1.09	1.02–1.07
Light oil for motor fuel	gal.	2.5–3.0	2.5–3.0	None
Ammonium sulphate	lbs.	25–30	10–12	12–18

Coal Gas.—This most volatile fraction of the distillation of "soft" coal is a valuable fuel. It is largely hydrogen and methane, with a little ethylene, benzene, etc. Its composition varies with the coal and the temperature and the rapidity of coking (Fig. 114). Higher temperatures favor decomposition of the hydrocarbons, increasing the percentage of hydrogen and reducing

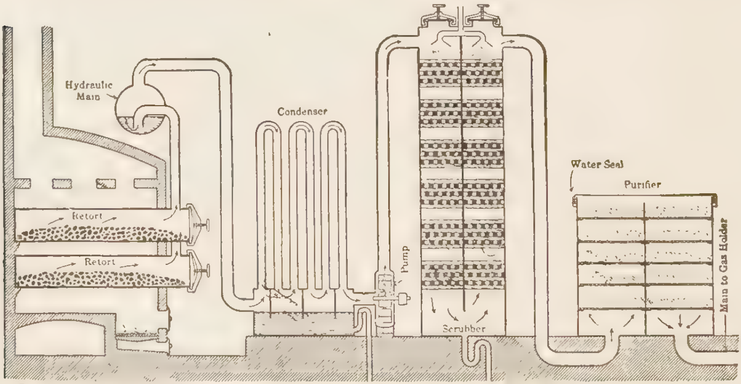


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FIG. 114.—Coal gas.

the illuminating power, but greatly increasing the volume of gas. Nearly half this gas is used to heat the retorts, but where the local market justifies it, the cheaper producer gas may be used for retort heating, thus releasing the entire output of coal gas for the market.

Coal gas is now piped 450 miles in Germany. Why not coke our own coal at the mines?

In some sections of Europe coal gas was valued as low as 11 cents per 1000 cubic feet, a price much below anything possible here.

ONE TON COAL	Gas, 10,000 cu. ft.	Benzene, 10–20 lbs. (largely washed out of the gas). Toluene, 3 lbs. Xylene, 1.5 lbs.
	Ammonium sulfate, 7–25 lbs.	
	Tar, 120 lbs.	Phenol, 0.5 lb. Naphthalene, 0.27 lb. Anthracene, 0.25 lb. Pitch, 80 lbs.
	Coke, 1200–1500 lbs.	

Water Gas.—Water gas is prepared by burning coke with a forced draft of air until the bed of coke is almost white-hot (Fig. 115). The carbon dioxide formed is allowed to waste. Next, the air is shut off and steam forced through the coke for five or six minutes. At about 1000° the reaction proceeds, but when the coke falls much below this temperature the reaction stops. The

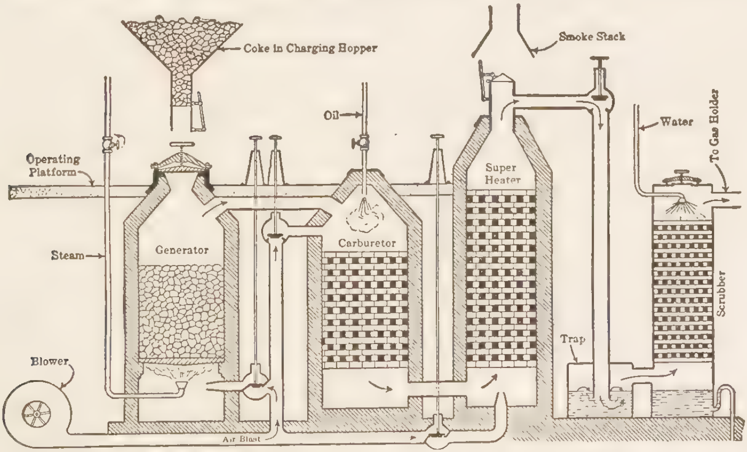
Coke in Charging Hopper
Smoke Stack
Oil
Water
To Gas Holder
Operating Platform
Super Heater
Steam
Generator
Carburetor
Scrubber
Trap
Blower
Air Blast

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FIG. 115.—Water gas.

steam is then shut off and air turned on until the coke is again nearly white-hot. The generation of water gas is intermittent:

$$C + H_2O \longrightarrow CO + H_2.$$

This gas is much used for domestic cooking and lighting by cities, although coal gas is rapidly gaining in competition. Water gas has good heating value, but is useless for lighting purposes unless used in connection with Welsbach mantles, because the flame is nearly colorless. Some states require a certain candle power of public gases and hence the present custom is to pass the gas through a cylinder containing hot brickwork on which a cheap petroleum oil is sprayed. The mixture then goes to a "superheater" of similar design where the brickwork is hot enough to "crack" the saturated hydrocarbons of the enriching oil. Thus the unsaturated ethylene and acetylene are formed and they confer high illuminating value on the lean gas. Methane and other hydrocarbons are also added by this process. Water gas is extremely poisonous before burning, due to its carbon monoxide content, so small leaks in flexible gas tube connections are dangerous. Why are its products of combustion non-poisonous?

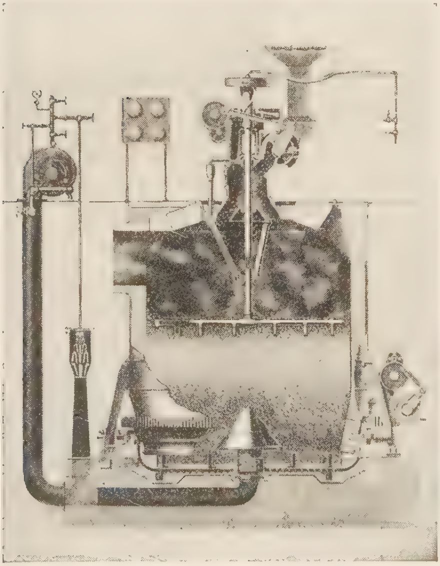

FIG. 116.—The Chapman gas producer. Note the introduction of steam and air at the bottom.

Producer Gas.—In a bed of coal five or six feet deep, the lower layers may be red-hot while the upper layers are not burning at all, possibly only suffering distillation of their volatile matter. If no flame plays over the surface, the escaping gas has good fuel value. Carbon dioxide formed in the lower layers is reduced, by the excess of hot carbon above, to the valuable carbon monoxide. All the nitrogen of the air used is found in the producer gas, making up nearly half its volume, hence the heating value is low—but the cost is also low. The best economy is to use this gas while it is still hot, thus saving all its sensible heat. In other words, it does not pay to pipe it to a distance. Even lignite can be converted into producer gas.

A "semi-water gas" is now made by blowing some steam with the air through the deep fuel bed in the producer gas process (Fig. 116). Reaction with the steam adds hydrogen and more carbon monoxide.

Blast Furnace Gas.—This is a sort of producer gas taken from the top of a blast furnace in iron making. Here we have a blast of air rising through a deep bed of coke and iron oxide. The product is a mixture of nitrogen, carbon dioxide, and carbon monoxide. About one-fourth of the mixture has fuel value and is used in the plant to operate gas engines or to raise steam.

Oil Gas.—Petroleum distillates may be " cracked " by heating in absence of air to form fuel and illuminating gases. Such products are known as "pintsch gas," "blau gas," etc. Railway trains have been lighted by cylinders of compressed pintsch gas. In 1929 the United States manufactured 150 billion cubic feet of the various fuel gases, doubling productions in eight years.

Liquid Fuels from Coal (Bergius and Other Processes).—At the present time there is world-wide interest in the hydrogenation of bituminous coal to yield liquid fuels suitable for motors. The process developed in Germany by Bergius is the most promising. Pulverized coal, mixed with heavy oil or tar to form a paste, is heated with hydrogen in a steel autoclave to 400° C. under 150-200 atmospheres pressure. The black tarry liquid resulting is then distilled up to 300° C. yielding about 15 per cent of motor fuel, 15 per cent Diesel engine fuel, 20 per cent gas and other products as listed below by Bergius for a coal of 6 per cent ash.

Products from 1 Ton of Coal

(*Quoted from Bergius, 1925*)

Motor fuel	42 gal.
Diesel-engine fuel	56 "
Lubricating oil	17 "
Fuel Oil	22 "
Gas	10,000 cu. ft.
Ammonia (NH_3)	10 lbs.
Coke residue	500 lbs.

Bergius points out the necessity of adding hydrogen to the coal because the ratio of hydrogen to carbon in the liquid fuels is double that in the coal itself. One ton of dry coal requires 35,000 cubic feet of hydrogen (10 per cent by weight) and less than half the hydrogen used actually reacts.

Fischer in Germany is preparing a mixed motor fuel called "synthol" by distilling off volatile matter from coal, passing steam over the resulting coke at about 1000° C. to make ordinary water gas ($C + H_2O \longrightarrow CO + H_2$), and finally heating the water gas at 150 atmospheres and 400° C. in presence of a catalyst (iron oxide impregnated with alkali). The product is a complex mixture of liquid hydrocarbons, aldehydes, ketones, methyl alcohol, and other alcohols up to one containing nine carbon atoms. A typical reaction is:

$$14\,CO + 16\,H_2 \longrightarrow 2\,C_5H_{11}OH + 4\,CO_2 + 4\,H_2O.$$

Our lignite reserves (chiefly in South Dakota) are estimated at 940,000,000,000 tons, from which, by the modern methods described above we could eventually make 12,000,000,000 barrels of motor fuel.

Powdered Coal Fuel.—The use of pulverized coal, blown into the furnace as a dust jet and burning with a long flame, has grown rapidly in recent years because every little particle is completely burned. As now prepared a cubic inch of coal yields a powder containing over 2,000,000,000 particles. Since this coal dust is blown into the furnace with a stream of air, perfect contact between coal and oxygen is secured with almost instantaneous combustion. Naturally there is no smoke. This fuel is used in burning Portland cement clinkers, roasting copper ores, melting metals, and, to an increasing extent, under steam boilers.

Smoke.—Smoke is made up of dust or dirt particles from the burning of fuels. Usually these particles are black carbon or tar although some ash is also carried into the air. The considerable fuel loss from such incomplete combustion may be nearly cancelled by the use of automatic stokers but when this is done the smoke from poorly stoked domestic fires remains obnoxious. Smoke makes cities ugly, kills vegetables, increases cleaning costs for clothing and furniture, and painting costs for buildings, shuts out the health-giving ultra-violet rays of the sun and, in general, makes life less attractive. The remedy is more general use of

Comparison of Industrial Gases

		Coal Gas	Enriched Water Gas	Producer Gas	Blast Furnace Gas	Oil Gas
Hydrogen,	H_2	49.8%	37.7%	13.2%	3.5%	13.5%
Methane,	CH_4	29.5	10.0	4.0	0.2	46.5
Ethane,	C_2H_6	3.2	3.2			3.9
Ethylene, etc.	C_2H_4	4.0	13.3			31.3
Carbon monoxide,	CO	8.5	30.4	25.3	26.5	2.4
Carbon dioxide,	CO_2	1.6	3.0	5.4	12.8	0.3
Nitrogen	N_2	3.2	2.1	55.2	56.9	1.1

automatic stokers in industry, electrification of railways (at least in and near large cities), invention of small, inexpensive automatic stokers for houses, use of oil-fired furnaces, and the piping of coal gas from the mines or central by-product coke oven plants. In Germany coal gas is now piped 450 miles. Civilization will greatly benefit by any or all of these forward steps.

A "B. T. U." is the amount of heat required to raise one pound of water 1° F.

As to cost, if in your city coal gas sells at 60 cents per thousand cubic feet, then coal of 12,000 B.T.U. heating value costing $24.00 per ton would be just as cheap. However you pay much less than this for "soft" coal. Other factors such as less dust and dirt, less work and a more even temperature control make gas and oil attractive as domestic fuels.

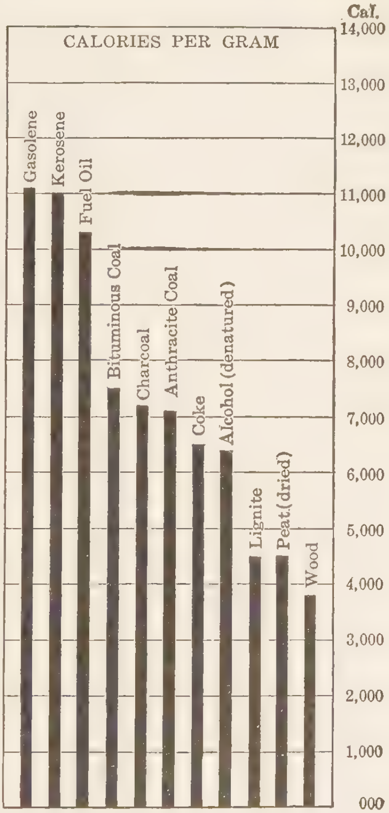

Fig. 117.—Fuel chart, calories per gram.

FUEL VALUES IN BRITISH THERMAL UNITS

Best bituminous coal	14,000 per pound
Anthracite coal	14,400 per pound
Lignite coal	8000–11,000 per pound
Coke	14,000 per pound
Coal gas	600 per cubic foot
Enriched water gas	500–600 per cubic foot
Producer gas	145 per cubic foot
Oil gas	300 per cubic foot
Fuel oil	19,800 per pound

THE EQUIVALENT COSTS OF DOMESTIC FUELS
(*Cross*)

Corresponding selling price of fuels to furnish an equal number of heat units for $1.00

NATURAL GAS AT 900 BTU PER CU. FT.	DOMESTIC COAL AT 12,000 BTU PER POUND	OIL DISTILLATE AT 140,000 BTU PER GALLON	COAL GAS 600 BTU per CUBIC FOOT	WOOD AT 8,500 BTU PER POUND	ELECTRICITY 3415 BTU PER K. W. HOUR
Per M cu. ft.	Per ton	Per gallon	Per M cu. ft.	Per cord	Per K. W. hour
$0.10	$ 2.67	$0.0156	$0.07	$ 2.30	$0.28
.20	5.34	.0311	.13	4.60	.56
.30	8.00	.0467	.20	6.90	.84
.40	10.68	.0612	.26	9.20	1.12
.50	13.35	.0780	.34	11.50	1.40
.60	16.00	.0933	.40	13.80	2.75
.70	18.67	1.089	.47	16.10	2.00
.80	21.36	1.224	.52	18.40	2.27
.90	24.00	1.400	.60	20.70	2.55
1.00	26.70	1.560	.68	23.00	2.83

Flames.—The shape of a flame is determined by the boundary between two gases which are reacting with evolution of light and heat. It does not matter whether a jet of hydrogen burns in an atmosphere of oxygen or a jet of oxygen burns in an atmosphere of hydrogen. The shape of the flame and the products are the same. It may be objected that solids also burn, but when flame is produced, as with wood or coal, it will be found that inflammable gases are distilling from the solid. Thus the flame of a candle is a gas flame. At the tip of the ordinary kerosene lamp-wick the heat of the flame distills the liquid into gas. Products of combustion may be solids, as with burning iron; liquids, as with burning hydrogen (after cooling); or gases, as with carbon monoxide.

A simple two-zone flame results when such a gas as hydrogen or carbon monoxide burns in air. The inner zone is of unburned gas and the outer zone is the burning zone. But with hydrocarbons flames of at least three zones result. This is to be expected when we remember that hydrocarbons are "cracked" or decomposed by heat. There must be a zone of decomposition into ethylene, hydrogen, etc. This may be illustrated by using a Bunsen burner with air inlets open; the inner bluish-green cone, *A*, is sharply defined. With less air admitted, a luminous cone, *B*, envelops this, while surrounding both is a sheath of perfectly burned gases, *C*, almost invisible (Fig. 118).

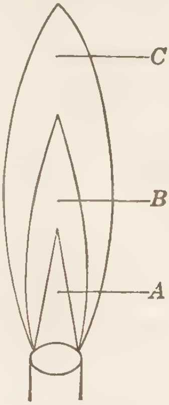

FIG. 118.

Smithells made clear that in *A* there is a little burning of the gas, as some carbon monoxide is present there, but cracking of the hydrocarbons into ethylene, acetylene, and hydrogen also occurs. In *B* (luminous cone) the carbon monoxide and hydrogen are burned, while the ethylene and acetylene are cracked into hydrogen plus carbon. It is largely due to the incandescence of this free carbon that the flame is luminous. A cold dish pressed into this zone becomes coated with carbon, since the carbon is cooled below its kindling temperature. The student should recall similar experiments with the flames of hydrogen sulfide, arsine, and stibine. (What were they?) Finally the hydrogen and carbon are completely burned in the outer sheath *C*.

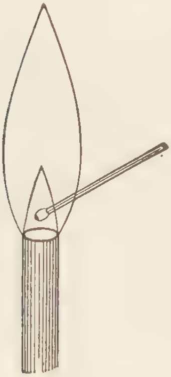

FIG. 119.

There is a small cone of unburned gas at the tip of the burner and a match head may be held in this without ignition (Fig. 119). A tube of small bore and about 8 cm. long may be inserted into this zone. The gas tapped off burns at the end of the tube if ignited.

The hottest parts of a flame are just above the tip of *B* and about the middle of the outer sheath. Here the Bunsen flame reaches 1560° or 1570°. At the top of the burner the temperature is only 300°. When too much air is admitted to the base of the Bunsen burner the "ignition wave" sometimes travels downward faster than the gas flows upward. The result is that the flame *strikes back* and burns down in the Bunsen tube with unpleasant odor and decided heating of the metal. The Meker burner prevents this by a heavy metal grid on top which cools any ignition wave so that the flame cannot run down the tube. Consequently much air may be admitted at the base and hotter flames obtained (as high as 1775°).

Safety Lamp.—The principle of the Meker grid (Fig. 120) can be shown by thrusting a wire gauze halfway down on a flame. No flame appears above the gauze simply because the gas is cooled below its ignition temperature. The gas passing through the gauze can be ignited by a match. Sir Humphry Davy in 1815 surrounded the coal miner's lamp with a heavy gauze and thus made it safe to carry such a lamp into coal mines containing fire damp (methane). Any methane diffusing through the gauze burns on the inside of the cage, but not on the outside, as the gauze chills the gas below its ignition point.

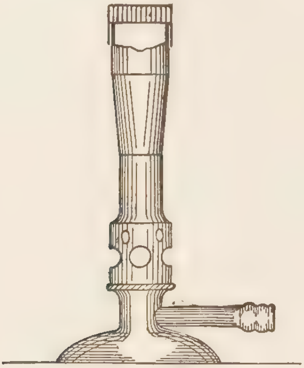

Fig. 120.—The Meker burner.

Welsbach Mantles.—These fabrics, containing 99 per cent thorium oxide and 1 per cent cerium oxide, become incandescent. Any moderately hot flame inside such a mantle produces intense light, several times as much as if the same gas were burned in an open jet, the old-fashioned way. The world uses two or three hundred million of these mantles annually.

Flame Colors.—Flames may be colored green, crimson, yellow, etc., by volatilizing in them certain metallic salts, preferably chlorides, since they are the most volatile of all salts.

EXERCISES

2. What are the natural sources of hydrocarbons?
3. Can we make hydrocarbons?
4. Why not use coal tar as a fuel?
5. If a gas containing some sulfur compounds were burned, would the products of combustion be unsafe in the house? Why?
6. Could a water gas plant and a coal gas plant coöperate to advantage?

7. What were the most valuable petroleum products twenty years ago? What are they to-day?

8. What will replace petroleum when it is exhausted?

9. Ten cc. of a gaseous hydrocarbon (call it C_xH_y) are exploded with an excess of oxygen. The volume contracts 30 cc. After the explosion the resulting gases are shaken with sodium hydroxide solution. A further contraction of 20 cc. is observed. What is the molecular formula of the hydrocarbon? Remember that 10 cc. of all gases (standard conditions) contain the same number of molecules.

10. A candle weighing 45 g. consists of wax composed of 85 per cent carbon and 15 per cent hydrogen. What weight of (*a*) carbon dioxide and (*b*) water will be formed by burning 40 per cent of the candle?

11. How many g. of aluminum carbide (Al_4C_3) would react with water to form 50 liters of methane at 15° and 740 mm.?

12. What volume of CO_2 is formed by the combustion of 10 g. of C_2H_2?

13. When benzene is ignited, the carbon is converted into carbon dioxide and the hydrogen into water. What weight of air would be required for the combustion of 100 g. of this hydrocarbon?

14. When 50,000 cubic feet of natural gas (consider it as methane, CH_4) are burned in the gas furnace how many liters, and gallons, of water could be condensed (if desired) by chilling the flue?

15. There are three possible isomeric pentanes and these are known (C_5H_{12}). Give their structural formulas, maintaining valences of four for carbon and one for hydrogen.

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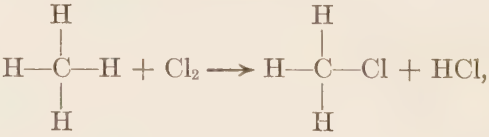
CHAPTER XXX

ALCOHOLS, ACIDS, FATS, AND SOAPS

There are 225,000 compounds of carbon, called "organic" compounds because prior to 1827 it was thought that they were organized or built up only in living animal or plant tissue. It was in 1827 that Wöhler synthesized urea in the test tube and thus started an era of laboratory organic syntheses that has given the world almost countless useful substances never known in nature. It is a remarkable fact that there are only 26,000 compounds other than those of carbon. We live in a carbon system and a water system but others are conceivable.

Organic chemistry is fundamental to biology, physiology, medicine, pharmacology, and agriculture, yet the sheer beauty of logical reasoning involved in its study would alone justify the development of the subject.

Derivations of the Hydrocarbons.—Methane slowly reacts with chlorine, first one atom of hydrogen being replaced by chlorine and, with longer treatment, all four hydrogen atoms being replaced.



$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-H + Cl_2 \longrightarrow H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-Cl + HCl,$$

$$CH_4 + Cl_2 \longrightarrow HCl + CH_3Cl, \text{ methyl chloride,}$$
$$CH_3Cl + Cl_2 \longrightarrow HCl + CH_2Cl_2, \text{ methylene chloride,}$$
$$CH_2Cl_2 + Cl_2 \longrightarrow HCl + CHCl_3, \text{ chloroform,}$$
$$CHCl_3 + Cl_2 \longrightarrow HCl + CCl_4, \text{ carbon tetrachloride.}$$

Ethane reacts with chlorine in the same way:

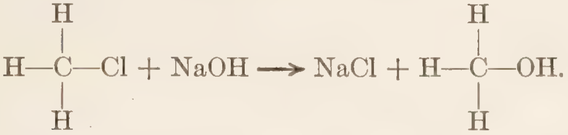
$$C_2H_6 + Cl_2 \longrightarrow HCl + C_2H_5Cl, \text{ ethyl chloride.}$$

It will be noted that a new group is found in methyl chloride, the monovalent ***methyl*** group (CH_3). Also in ethyl chloride is found the monovalent ***ethyl*** group (C_2H_5). Chloroform and carbon tetrachloride are not made commercially by the above methods, but they may be so prepared. Methyl, ethyl, propyl and similar radicals are called "alkyl" groups.

Starting with methyl chloride (which does not ionize as does sodium chloride), we can make ***methyl alcohol*** very simply (but not profitably). ***Ethyl alcohol*** can be formed in a similar manner:

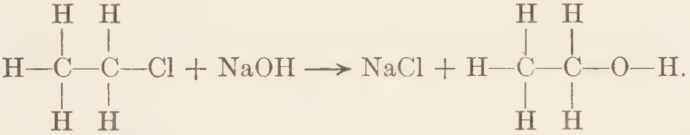
$$CH_3Cl + NaOH \longrightarrow NaCl + CH_3OH,$$
$$C_2H_5Cl + NaOH \longrightarrow NaCl + C_2H_5OH.$$

As it happens, there are better methods of preparing these important and famous (or infamous) alcohols, but this one is valuable in showing us the structure of alcohols.



$$\begin{array}{c}H\\|\\H—C—Cl\\|\\H\end{array} + NaOH \longrightarrow NaCl + \begin{array}{c}H\\|\\H—C—OH.\\|\\H\end{array}$$

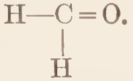
Knowing the structure of methane to begin with, the structure given for methyl chloride follows, and hence we are positive that in methyl alcohol the hydroxyl radical must be attached directly to the same carbon atom that holds the other hydrogen atoms. By the same logic we are confident that the structural formulas given in the following equation are correct:



$$\begin{array}{c}H\quad H\\|\quad\ |\\H—C—C—Cl\\|\quad\ |\\H\quad H\end{array} + NaOH \longrightarrow NaCl + \begin{array}{c}H\quad H\\|\quad\ |\\H—C—C—O—H.\\|\quad\ |\\H\quad H\end{array}$$

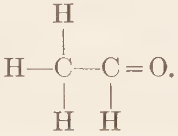
Having learned the general structure of alcohols, we can now proceed to show what will happen if we oxidize them (as with sodium dichromate and sulfuric acid):

$$CH_3OH + O_2 \longrightarrow H \cdot CHO. \quad \text{Structure,}$$



$$\begin{array}{c}H—C=O\\|\\H\end{array}$$

$$C_2H_5OH + O_2 \longrightarrow CH_3CHO. \quad \text{Structure,}$$

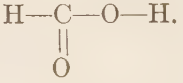


$$\begin{array}{c}H\\|\\H—C—C=O.\\|\quad\ |\\H\quad H\end{array}$$

Thus we see that two hydrogen atoms are removed from each molecule of an alcohol yielding as oxidation products, ***aldehydes,*** the first being formaldehyde, $H \cdot CHO$, and the second, acetaldehyde, $CH_3 \cdot CHO$. In each, and indeed in all aldehydes, the same group (—CHO) is found, so if "R" stands for any radical, CH_3— or C_2H_5—, etc., we might clearly represent any adehyde as $R \cdot CHO$.

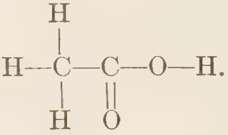
More vigorous oxidation of alcohols or of aldehydes produces another familiar class of compounds, the ***organic acids.***

$CH_3OH + O_2 \longrightarrow H \cdot COOH$. Structure,



$$\mathrm{H{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O{-}H.}$$

$C_2H_5OH + O_2 \longrightarrow CH_3 \cdot COOH$. Structure,



$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O{-}H.}$$

The first is formic acid, $H \cdot COOH$, and the second is acetic acid, $CH_3 \cdot COOH$. In all organic acids we find the same carboxyl group (—COOH). An important point to remember is that in these acids it is only the hydrogen atom in each carboxyl group that ionizes. The hydrogen atoms in the radicals never ionize. This is why the formula for acetic acid is frequently written as $H \cdot C_2H_3O_2$, setting apart the ionizable hydrogen. However, we prefer to use its halfway structural formula, $CH_3 \cdot COOH$.

CHLORINE DERIVATIVES	ALCOHOLS	ALDEHYDES	ACIDS
Methyl chloride, CH_3Cl	Methyl alcohol, CH_3OH	Formaldehyde, $H \cdot CHO$	Formic acid, $H \cdot COOH$
Ethyl chloride, C_2H_5Cl	Ethyl alcohol, C_2H_5OH	Acetaldehyde, $CH_3 \cdot CHO$	Acetic acid, $CH_3 \cdot COOH$
Propyl chloride, C_3H_7Cl	Propyl alcohol, C_3H_7OH	Propylaldehyde, $C_2H_5 \cdot CHO$	Propionic acid, C_2H_5COOH
Butyl chloride, C_4H_9Cl	Butyl alcohol, C_4H_9OH	Butylaldehyde, C_3H_7CHO	Butyric acid, $C_3H_7 \cdot COOH$
$R \cdot Cl$	$R \cdot OH$	$R \cdot CHO$	$R \cdot COOH$

EXERCISE 1.—Start with propane and show, step by step, how to make an acid from it. Give the exact structure of each compound.

EXERCISE 2.—From what hydrocarbon could you make acetic acid? Give the steps.

The Alcohols.—The alcohols remind us of inorganic bases in their structure but not in their action:

$$\begin{aligned}&(1)\ C_2H_5Br + KOH \longrightarrow KBr + C_2H_5OH,\\&(2)\ NH_4Br + KOH \longrightarrow KBr + NH_4OH.\end{aligned}$$

There is a good deal of similarity between the above reactions, but there is this fundamental difference. Reaction (2) is between ions, but ethyl bromide (C_2H_5Br) does not ionize, so it reacts as a molecule. When the products are examined it is found that the ethyl hydroxide or ethyl alcohol does not affect litmus paper, does not conduct electricity, and, in short, does not ionize at all. It appears, then, that a hydroxyl group attached directly to a hydrocarbon radical has very different properties (alcoholic) from a hydroxyl group attached directly to a metal (basic) or even to a non-metal (acidic). Any simple alcohol may be represented by the general formula $R \cdot OH$, where "R" is CH_3, C_2H_5, etc.

Methyl Alcohol (Methanol), CH_3OH.—In commercial practice this alcohol is made by the retort distillation of wood, hence its common name, "wood alcohol." The distillation of wood to yield charcoal parallels the distillation of coal to yield coke. As with coal the volatile by-products were wasted in former years, but now they are in great demand. Acetic acid and acetone are among the products of wood distillation.

In 1924 the French and the Germans developed a catalytic process for preparing methyl alcohol by the direct union of carbon monoxide and hydrogen under considerable pressure in the presence of zinc oxide and copper.

$$2\ H_2 + CO \longrightarrow CH_3 \cdot OH.$$

A very pure product was prepared in commercial quantities at a cost comparable to that of wood distillation. It is barely possible that this liquid fuel may compete with gasoline at some time in the future.

Methyl alcohol (CH_3OH) is a colorless liquid boiling at 67.4°, miscible with water in all proportions, intoxicating, and extremely poisonous. Blindness is a common result of a methyl alcohol debauch. In fact, continued exposure to its vapor or contact with the skin is detrimental. Since it is used to "denature" ordinary grain alcohol, there is a real danger in failure to remember the poisonous properties of methyl alcohol. Wood alcohol is much used as a solvent in varnishes and as the starting point in the manufacture of formaldehyde.

Ethyl Alcohol (Ethanol), C_2H_5OH.—Ethyl alcohol (C_2H_5OH), commonly known as "grain alcohol," is a colorless, inflammable liquid boiling at 78° and is miscible with water in all proportions. It is not poisonous, although when taken to excess in strong beverages the effect on the system is distinctly injurious. Like fire, alcohol is a good servant, but a bad master. As a servant it is one of the best solvents in the laboratory and the starting point in the manufacture of many useful compounds. Internal-combustion motors can use it, with certain adjustments, and when our coal and oil deposits are exhausted the world will probably turn to cheap alcohol as a power fuel. It can be made from the starch and cellulose and sugars of plants, hence the sun's heat and power can be utilized in this way.

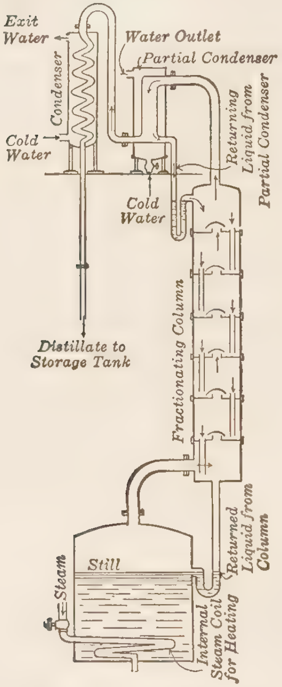
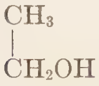

Exit Water
Water Outlet
Partial Condenser
Condenser
Cold Water
Returning Liquid from Partial Condenser
Cold Water
Fractionating Column
Distillate to Storage Tank
Still
Steam
Returned Liquid from Column
Internal Steam Coil for Heating

FIG. 121.—Commercial still with fractionating column. The more readily condensed water vapors return to the still while the more volatile alcohol vapors reach the condenser.

Alcohol fermentation of sugars supplies us with all the ethyl alcohol used. Glucose is the only common fermentable sugar, so cane sugar, malt sugar, starch, and cellulose must all be converted into glucose before they can yield alcohol. The reactions involved will be given later. We produce about 100,000,000 gallons annually.

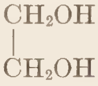
Alcohol as a solvent and as a raw material is indispensable to chemical manufacture. It is essential to the manufacture of many dyes, lacquers, explosives, cosmetics, and medicines. Surgery without alcohol would do without the great anæsthetics ether, chloroform, and ethylene, which are made from alcohol. Iodoform is made from this much-maligned substance and alcohol itself is strongly antiseptic. Furthermore, the surgeon or physician hurrying to his patient in cold weather is glad to have in the radiator of his auto some alcohol, as one of the best anti-freeze substances known.

Other Alcohols.—*Glycerine* (glycerol, to be exact) is an alcohol, although we are inclined to forget that fact, since it is non-intoxicating. Its structure shows the presence of alcoholic hydroxyl groups, three of them in each molecule. Glycerol is a colorless, syrupy liquid of sweetish taste. Since it is hygroscopic (deliquescent) it keeps moist and is often put in mixtures because of this property. A great deal is used in plug tobacco and in some medicinal preparations, but most of it is converted into nitroglycerine. Both glycerol and glycol are much used in anti-freeze solutions for autos. When fats are broken down in soap making, glycerol is a by-product. The same alcoholic hydroxyl is found in the sugars. A comparison of structural formulas of ethyl alcohol, glycerol, and a typical sugar such as glucose is interesting. Ethyl alcohol may be represented as C_2H_5OH or $CH_3 \cdot CH_2OH$.



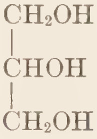
$$\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CH_2OH} \end{array}$$

Alcohol



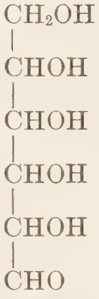
$$\begin{array}{l} \mathrm{CH_2OH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

Glycol



$$\begin{array}{l} \mathrm{CH_2OH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

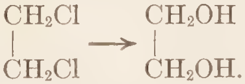
Glycerol



$$\begin{array}{l} \mathrm{CH_2OH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CHO} \end{array}$$

Glucose

Glycol, very similar in properties and structure to glycerol, is now made in large quantities by cracking natural gas to ethylene, adding chlorine to the molecules of ethylene and hydrolyzing to glycol.



$$\begin{array}{l} \mathrm{CH_2Cl} \\ | \\ \mathrm{CH_2Cl} \end{array} \longrightarrow \begin{array}{l} \mathrm{CH_2OH} \\ | \\ \mathrm{CH_2OH.} \end{array}$$

Alcohols from Petroleum.—The enormous demand for certain alcohols and their esters as solvents for cellulose lacquers and varnishes has led to the synthesis of isopropyl, secondary butyl and secondary amyl alcohols from hydrocarbons. Cracked gasoline contains some unsaturated hydrocarbons (olefines or the ethylene series) which react with concentrated sulfuric acid to form alkyl esters. These esters are then hydrolyzed with water to form the alcohols. Pentane has also been chlorinated and the chlorine replaced with hydroxyl to form amyl alcohol. The higher alcohols up to decyl will, doubtless, soon be obtained, in much smaller quantities, from the petroleum cracking process. Butyl alcohol ("butanol") is now produced by a special fermentation of corn starch to the extent of over 20,000,000 pounds yearly in the United States. Over 27,000,000 pounds of butyl acetate are made for the solvent industry.

Cellulose lacquers (over 15,000,000 gallons annually in this country) are rapidly replacing paints and varnishes, notably in finishing automobiles.

Ethers.—The ether we know as an anæsthetic is produced by the action of hot concentrated sulfuric acid in removing the elements of water from alcohol.

$$(1)\quad C_2H_5OH + H_2SO_4 \longrightarrow C_2H_5OSO_3H + H_2O,$$
$$(2)\quad C_2H_5OSO_3H + C_2H_5OH \longrightarrow (C_2H_5)_2O + H_2SO_4.$$

This diethyl ether, $(C_2H_5)_2O$, is a colorless liquid of very low boiling point, 35°, very inflammable, and only slightly soluble in water. It is a useful solvent for a great number of substances. Dimethyl ether is $(CH_3)_2O$ and any ether could be represented as R_2O.

Aldehydes.—Wood alcohol can be oxidized moderately enough to fall short of becoming formic acid and thus formaldehyde may be secured. Other aldehydes are made in similar fashion. They are all reducing agents.

$$CH_3OH + (O) \longrightarrow H\cdot CHO + H_2O.$$

In practice the vapors of methyl alcohol, mixed with air, are passed through a tube containing heated copper gauze as the catalyst:

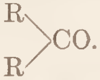
Formaldehyde is used as a 40 per cent solution called formalin. It is a much used germicide and antiseptic. A large amount, 30,000,000 pounds annually, is used to react with phenol (carbolic acid) in the preparation of "***bakelite***," a substitute for hard rubber. "Substitute" is a poor name here, for bakelite is superior to the hard rubber. By the use of formaldehyde, other similar plastics are made, such as "redmanol," etc. We see these useful materials as telephone receivers, handles for toilet articles, buttons, electric insulation material, fountain pens, pipe stems, and scores of familiar articles. "Pollopas," a new synthetic resin, very permeable to ultra-violet light, is a condensation product of formaldehyde and urea. Read the surprising chapter on Synthetic Plastics in Slosson's *Creative Chemistry.*

A comparison of the formulas of the various aldehydes in the series ($H \cdot CHO$, $CH_3 \cdot CHO$, $C_2H_5 \cdot CHO$, etc.) shows that they all contain the characteristic group, —CHO. Thus the general formula for all aldehydes may be written $R \cdot CHO$, in which R represents any radical such as methyl (CH_3) or ethyl (C_2H_5).

Furaldehyde is a recent commercial product made from various wastes such as oat hulls and corn cobs. It is a good solvent, can be made into synthetic resins and has both germicidal and fungicidal properties.

Acetone, $(CH_3)_2CO$.—This colorless liquid is used as a safe solvent for compressed acetylene and in the manufacture of chloroform. It is a solvent for many substances, such as fats and varnish materials, and is of very great importance as a solvent in the manufacture of cordite and the various smokeless powders. During the early part of the World War there was a wild scramble to get enough acetone. A huge "quick vinegar" plant was installed and the acetic acid converted into calcium acetate, which was then distilled for acetone. Every source was utilized. By another process acetylene was catalytically converted into acetaldehyde, this into acetic acid, and the acid into acetone by the calcium acetate step. Acetone is now made almost entirely by the fermentation of corn through the action of a very useful bacteria (*clostridium acetobutylicum*). Normal butyl alcohol is formed at the same time.

Acetone is merely the simplest member of a series of ***ketones*** whose general formula is



$$\begin{matrix} R \\ R \end{matrix} \!\! > CO.$$

Acids.—There are different series of organic acids, but the "fatty-acid" series is the one of most common interest. The fats contain glycerine compounds of some of these acids, hence the name. All the members of this series are monobasic. Most of them are liquid, but such acids as palmitic and stearic are solids. Formic and acetic acids are the simplest members and the general formula may be written $R \cdot COOH$.

Formic Acid, $H\cdot COOH$.—Formic acid, $H\cdot COOH$, is found in stinging nettles and red ants, adding zest to the sting or bite. It may be made by sufficient oxidation of methyl alcohol, but there is little demand for the acid.

Acetic Acid, $CH_3\cdot COOH$.—The world has always known acetic acid, at least in mixtures, for the fermentation of sugar in fruits has always produced alcohol, and this in contact with the proper organism (*mother of vinegar*) has always produced acetic acid. Vinegar contains about 4 per cent of acetic acid. Vinegars may be made from cider in a week or two if the *mother of vinegar*, which aids the oxygen of the air in uniting with the alcohol, is spread through a barrel of beechwood shavings (tasteless wood). Perforations in the barrel admit the necessary air and as the cider trickles through again and again, excellent contact is made. This was the process referred to in the discussion of acetone. As stated in connection with acetone a method has been devised for catalytically converting acetylene into acetaldehyde and acetic acid.

Acetic acid, when anhydrous, is a colorless liquid (***glacial acetic acid***) freezing to a crystalline solid at 18°. With water it forms a colorless solution. The odor is sharp and penetrating.

The anhydride of acetic acid, $(CH_3CO)_2O$, is essential to the manufacture of cellulose acetate silk, the best type of rayon. It is to be remembered in this connection that it is possible to convert acetylene ⟶ acetaldehyde ⟶ acetic acid ⟶ acetic anhydride.

Esters.—Alcohols react with organic acids to form water and esters. These esters remind us somewhat of salts in their method of formation (but not in properties) and hence are often called ***ethereal salts.*** A comparison of the reactions producing inorganic salts and ethereal salts helps clear up the relations.

$$(1)\quad CH_3\cdot COO\boxed{H} + K\boxed{OH} \longrightarrow H_2O + \underset{\text{Potassium Acetate}}{CH_3\cdot COOK},$$

$$(2)\quad CH_3\cdot COO\boxed{H} + C_2H_5\boxed{OH} \rightleftarrows H_2O + \underset{\text{Ethyl Acetate}}{CH_3\cdot COOC_2H_5}.$$

Reaction (1) is neutralization of an acid by a base. A hydrogen ion from the acid unites with the hydroxyl ion from the base to form water. But reaction (2) is not neutralization, since the alcohol does not yield hydroxyl ions. All we can say is that the

hydroxyl group of the alcohol unites with the ***acidic hydrogen*** of the acid to form water and that the hydrocarbon radical (C_2H_5) of the alcohol replaces the acid hydrogen of the acid, forming an ethereal salt, in this case ethyl acetate. In general esters may be represented by $R\cdot COOR'$, where R and R′ are any hydrocarbon radicals. Inorganic acids also react with alcohols and the products are usually called esters also. Ethyl nitrate ($C_2H_5\cdot NO_3$) is the ethyl ester of nitric acid. (How formed?) The so-called nitroglycerine is really glyceryl trinitrate, an ester of nitric acid and the alcohol glycerine.

Most fruit flavors and odors are due to esters.

Exercise 3.—How could you make methyl propionate? Propyl butyrate?

Exercise 4.—Here is a chart comparison of typical organic compounds. Name each member.

Hydrocarbons	Halogen Derivatives	Alcohols	Aldehydes	Acids	Ethyl Esters
CH_4	$CH_3\cdot Cl$	CH_3OH	$H\cdot CHO$	$H\cdot COOH$	$H\cdot COOC_2H_5$
C_2H_6	$C_2H_5\cdot Cl$	C_2H_5OH	$CH_3\cdot CHO$	$CH_3\cdot COOH$	$CH_3\cdot COOC_2H_5$
C_3H_8	$C_3H_7\cdot Cl$	C_3H_7OH	$C_2H_5\cdot CHO$	$C_2H_5\cdot COOH$	$C_2H_5\cdot COOC_2H_5$
etc.	etc.	etc.	etc.	etc.	etc.

Fats.—The esters derived from glycerine (as the alcohol) and the higher fatty acids, such as palmitic and stearic (and oleic from a related series), are called fats. This means that fats are a particular kind of ester. We do not have to synthesize the fats—plants and animals have done that for us, but if desired it could be done:

$$\underset{\text{Glycerine}}{C_3H_5(OH)_3} + \underset{\text{Oleic Acid}}{3\ C_{17}H_{33}\cdot COOH} \longrightarrow \underset{\text{Clyceryl Oleate, a fat}}{(C_{17}H_{33}\cdot COO)_3C_3H_5} + 3\ H_2O.$$

There are very few simple fats in animal and plant tissue. Olive oil is largely glyceryl oleate ("olein") but lard is a mixture of 40 per cent glyceryl palmitate (palmitin) and stearate (stearin) with 60 per cent olein. Beef suet contains the same fats but is harder because it contains only 25 per cent olein. Olive oil and cottonseed oil are liquids because they contain fully 75 per cent olein. Butter is a mixture of several fats. When it becomes rancid with age some of the esters are decomposed, yielding free acid, and the offensive odor of butyric acid makes itself known.

Oleomargarine is a butter substitute in great demand. To make it, beef fat from which much stearin has been removed by crystallization at 24° is stirred with some oil to soften it, and churned with milk to give it the butter flavor. On chilling, the "oleo" separates. Vegetable fats are worked into "oleo" to make the "nut margarines."

Edible liquid fats are in great demand as salad oils and cooking oils. Olive oil is the most expensive, but recently enormous quantities of purified cottonseed oil, peanut oil, and corn oil have found a ready market. The United States produces nearly a billion pounds of cottonseed oil every year, yet all this was formerly wasted when cotton seed was thrown away.

Manchuria, yearly, produces four million *tons* of soya bean oil for soaps, food, etc., using the residual press cake as a good protein stock food or fertilizer. The United States planted 3,000,000 acres with this bean in 1929 and will rapidly increase this area. Peanut oil, produced in British African colonies to a value of more than $20,000,000 annually, has actually been used as a fuel in Diesel engines. The world's olive oil production is fully 2,000 million pounds. Tung oil, so essential as a rapid drying oil in the manufacture of certain varnishes and linoleum has been imported in poor condition from China (100,000,000 pounds yearly) but will now be produced in northern Florida. Over 200,000 tung nut trees have been planted there. The United States uses over 100,000,000 gallons yearly of linseed oil for paints, linoleum, etc.

Chaulmoogra oil from a nut on the rather rare tropical chaulmoogra tree has given the world a tool in the effort to cure leprosy. The fatty acids freed from that oil have been converted into new acids and esters a hundred times more potent towards leprosy than the natural product.

In the course of some recent important research on the chemistry of tuberculosis a new liquid fat combined with phosphoric acid was extracted from a factory-produced quantity of the tubercle bacilli. When this fat was injected into the animal body it caused tubercle lesions.

Soaps.—Esters are hydrolyzed by water, especially by hot water. The equilibrium reaction below indicates this:

$$CH_3 \cdot COOH + C_2H_5OH \rightleftarrows H_2O + CH_3 \cdot COOC_2H_5.$$

This hydrolysis takes place faster if a base is present. Of course a salt of the fatty acid must be formed.

$$\underset{\text{Glyceryl Oleate}}{C_3H_5(C_{17}H_{33}\cdot COO)_3}+3\ KOH \longrightarrow \underset{\text{Glycerine}}{C_3H_5(OH)_3}+\underset{\text{Potassium Oleate, a soap}}{3\ C_{17}H_{33}\cdot COOK}.$$

This reaction is called saponification of the ester and the salt of the fatty acid is called a soap. When a fat is saponified by hot water, glycerine and the free acid are the products. This reaction is catalyzed by the Twitchell reagent and the resulting fatty acids treated with Na_2CO_3 (cheaper than NaOH) to make soap. Soap-making on a commercial scale is usually a matter of boiling cheap mixed fats with caustic soda if the firm, "hard" soaps are desired, or with caustic potash if "soft" soaps are wanted. The soft soap of early pioneer days was made by using the lye (K_2CO_3) leached from wood ashes and such lard and tallow as accumulated about the house. Greater refinements are demanded now. Soap is "salted out" by common salt, partially dried and pressed into cakes. The remaining solution is distilled for its glycerine. By the Twitchell process fats are boiled with water and a complicated catalyst, yielding pure glycerine and the fatty acids. To make a soap from these acids is simply a matter of neutralization with a base.

If civilization is measured by the amount of soap used it must be significant that the United States makes and uses $250,000,000 worth annually.

EXERCISES

5. How many grams of glucose must be used to prepare 800 g. of alcohol, assuming the yield to be 90 per cent? What will be the volume of CO_2 evolved (Standard conditions)?

6. How many grams of the soap, potassium oleate, can be made from 45 grams of glyceryl oleate, $C_3H_5(C_{17}H_{33}\cdot COO)_3$?

7. What weight of acetone can be obtained by heating 157 g. of calcium acetate?

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CHAPTER XXXI

THE CARBOHYDRATES

A most important class of compounds, including starch, the sugars, and cellulose, contains carbon and just twice as many hydrogen atoms as oxygen atoms in each molecule. This means that the two latter elements are found in the proportion to form water, hence the name, carbohydrates. On heating, some of these give off water formed in the general decomposition but not held like water in hydrates. Plants take carbon dioxide from the air and water from the soil, building them into the cellulose of wood, cotton, linen, grasses, etc., or the starch of potatoes, arrowroot, cassava, rice, and the other roots and grains. Molecules of both starch and cellulose are probably large, represented by some multiple of $C_6H_{10}O_5$.

Cellulose.—Cellulose is more fully treated on page 415 but it may be stated here that this carbohydrate makes up half the weight of dry wood. Pure linen and cotton fibers as well as the stringy parts of many vegetables and grasses represent cellulose.

The hydroxyl groups react with acids so that water and cellulose esters form.

The reason our forest sources of paper pulp are rapidly being exhausted is the fact that every American citizen uses 150 pounds of paper annually. Spruce, hemlock, and balsam are among the woods favored for paper making.

Starch.—Starch is stored in roots like potatoes, in grains, in chestnuts, and in the trunk of the sago palm. It is a white substance of very high molecular weight $(C_6H_{10}O_5)_x$, insoluble in cold water, but swelling in hot water to a pasty translucent mass. When heated sufficiently it forms a yellowish, sweet substance called dextrin. The crust of bread (baked at a higher temperature than the moist interior) probably owes its sweetness to dextrin. Dextrin has been used as a mucilage on envelopes and postage stamps. Starch itself in the form of a paste is commonly used in hanging wall paper. It is a valuable food when cooked, but is far less digestible raw. Having alcoholic hydroxyl groups it can, of course, be nitrated. Nitro-starch is a very safe explosive and was used to the extent of thousands of tons in filling hand grenades. In the laundry, starch is indispensable. It is also one of the chief sources of ethyl alcohol. When treated with water and a trace of acid as a catalyst it is hydrolyzed into glucose.

The Sugars.—There are two important classes of soluble sugars, monosaccharides and disaccharides. The distinction is easy. Sugars of the formula, $C_{12}H_{22}O_{11}$, can be broken down into simple sugars, usually of the formula $C_6H_{12}O_6$. Such simple sugars cannot be resolved into still simpler sugars.

Complex sugars (Polysaccharides) $C_{12}H_{22}O_{11}$	Sucrose (cane sugar) Maltose (malt sugar) Lactose (milk sugar)
Simple sugars (Monosaccharides) $C_6H_{12}O_6$	Dextrose (glucose) or grape sugar Levulose (fructose) or fruit sugar Galactose Mannose Xylose, etc.

The sugars contain alcoholic hydroxyl radicals and, since there are several sugars of the formula $C_6H_{12}O_6$, there must be several different arrangements of the groups. The avocado pear contains a very unusual sugar, with seven carbon atoms in the molecule. Some of the rarer sugars are decomposed only by definite strains of bacteria and so are used in the recognition of these bacteria.

Sweetness is not the infallible test for "sugars." Saccharin is 500 times as sweet and perillaldehyde (alpha-antialdoxime) is 2000 times as sweet as sucrose, yet they do not have the structure of sugars, therefore are not sugars. Some "sugars," on the other hand, are not sweet. If sucrose is rated in a scale of sweetness as 100, levulose is 173, glucose (dextrose) 74, maltose 32, and lactose (milk sugar) 16.

The annual production of lactose from cows' milk is about 4,000,000 pounds, but this is only a small fraction of the possible production. Recently a more soluble form (apparently sweeter) called beta anhydride lactose has been put on the market.

At Yale, Johnson and Anderson have recently found a new sugar (isolated from a quantity of tubercle bacilli) that is harmless to an uninfected animal but poisonous to a tuberculous animal.

Sucrose, $C_{12}H_{22}O_{11}$.—Cane sugar, beet sugar, and maple sugar are all the same when purified.

Sugar from cane is produced in Cuba, Hawaii, Java, Brazil, and Louisiana—most of it in Cuba. The cane is crushed to extract the juice, which is then treated with lime to coagulate impurities that would otherwise ferment. The juice (12–18 per cent sugar) is next treated with carbon dioxide to precipitate the lime as calcium carbonate, or with phosphoric acid to precipitate calcium phosphate. The solution is boiled down in vacuum pans because if boiled at atmospheric pressure it would be decomposed. When the sugar crystallizes it is whirled free from molasses in centrifugals and shipped to refineries for further purification. (See Carbon Chapter.)

Sucrose turns yellow-brown on heating, forming caramel, much used to color various food products.

The sugar beet is grown on great areas of France, Germany, Russia, and in certain parts of the United States. This country makes 1,000,000 tons yearly from beets, but we eat 5,000,000 tons. Probably half the world's sugar is made from beets. There are certain special difficulties in extraction of the sugar, and the molasses is not palatable, but it is a profitable industry nevertheless. By careful breeding the sugar content of the beets has been increased to over 18 per cent.

Sucrose treated with acid as a catalyst reacts with water to form "invert sugar," a mixture of dextrose and levulose. Curiously enough, this mixture, with some delicious impurities, makes up the main part of honey:

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Dextrose}}{C_6H_{12}O_6} + \underset{\text{Levulose}}{C_6H_{12}O_6}.$$

In 1928 Pictet in Geneva reversed this reaction, synthesizing sucrose.

Glucose, $C_6H_{12}O_6$.—This is also called dextrose and even grape sugar, since it occurs in grapes and raisins. It is less sweet than sucrose, but is a perfectly good food; in fact it is partly digested cane sugar. Both starch and sucrose, all the complex sugars in fact, are converted into glucose by the digestive fluids. Glucose is made commercially from starch which is heated with water and some acid as a catalyst:

$$(C_6H_{10}O_5)_x + x\,H_2O \longrightarrow x\,C_6H_{12}O_6.$$

Hydrochloric acid is used in a 0.1 per cent solution. The trace of sodium chloride formed on neutralization with sodium hydroxide does no harm. Since corn starch is generally used as the raw material, the solution resulting is called "corn syrup." In addition to some water it contains 45 per cent of maltose, 20 per cent of glucose, and 35 per cent of dextrin. The dextrin prevents crystallization of the glucose. Some of the table syrups are largely corn syrup, with some added cane sugar and even maple sugar for flavoring. Over 40,000,000 bushels of corn are converted into about 900,000,000 pounds of glucose annually in the United States. One bushel of corn (60 pounds) yields 27 pounds of glucose (dextrose), 5 pounds crude molasses, 1 pound of corn oil and 27 pounds of gluten stock food. Glucose is used in candies, soda fountain syrups, baked goods, and even as a filler for cheap soaps and leather. As an intermediate compound in the manufacture of alcohol (as well as whisky and beer) from the starch of cereals glucose has been of vast importance.

Glucose reduces Fehling's solution, precipitating yellow-red cuprous oxide, a reaction very useful in medical diagnosis.

In recent years a pure white, well-crystallized dextrose (or glucose) has been put on the market.

Levulose and Inulin.—When inulin, a carbohydrate closely resembling starch, is hydrolyzed in similar manner levulose (fructose) is formed instead of dextrose (glucose). This sugar, as sweet as sucrose, is soon to be put on the market. Our Bureau of Standards has shown how to crystallize this very soluble sugar and although it is somewhat deliquescent it can be handled normally in block form, or, with slight precaution, in loose granulated form.

The problem of an adequate source of inulin has also been solved. The Jerusalem artichoke grows huge quantities of tubers on its roots, tubers rich in inulin. This artichoke is propagated by cuttings like potatoes and is adapted to the soil and climate of most of the United States. One variety has been found capable of yielding two tons of levulose per acre. It is to be hoped that large areas will be planted. Since freezing does not injure the tubers they can be stored to suit factory convenience. The Bureau of Standards believes that levulose can compete with the other sugars. Dahlia tubers also contain inulin.

Enzymes and Fermentation.—The yeast plant, a very lowly but useful organism made up of microscopic cells, secretes two chemicals known as invertase (or sucrase) and zymase. These are true catalysts. Enzymes differ from the inorganic catalysts in that they are compounds secreted by living organisms. Sucrase splits sugar (in the presence of water) into glucose and fructose, both fermentable, although fructose is less so than the glucose. Zymase finishes the work begun by the sucrase and converts the simple sugars into alcohol and carbon dioxide:

$$C_6H_{12}O_6 \longrightarrow 2\,CO_2 + 2\,C_2H_5OH.$$

It is an interesting fact that a germinating seed (barley, for example) develops enzymes as it sprouts. These catalysts, amylase and maltase, convert the insoluble starch of the seed into soluble glucose capable of being carried by the sap of the growing plant. The brewer borrows this clever device from the sprouting grain in order to make alcoholic drinks from starchy crereals. He allows barley to sprout, of course developing amylase and maltase in the process, then heats the sprouts to kill all life. The catalysts, mere chemicals, are uninjured. This "malt" is then mixed with the warm, moist, crushed grain and the starch is hydrolyzed to maltose, malt sugar, $C_{12}H_{22}O_{11}$. Yeast is then added and the malt sugar further hydrolyzed to form glucose. The zymase completes the change by fermenting this glucose into alcohol. By distillation a 45 per cent alcoholic solution well known as "whisky" is secured. Beer is simply the fermented liquor made from barley without distillation. Wine is fermented from grape juice by the wild yeast found on the skins of the grape. Even in as lawful a process as bread-making the yeast causes a fermentation with release of carbon dioxide and consequent "rising" of the dough.

Starch (by amylase) ⟶ maltose,
Maltose (by maltase) ⟶ glucose,
Glucose (by zymase) ⟶ alcohol.

There are other enzymes than those secreted by yeast or by sprouting grains. The animal body secretes enzymes which manage digestion of food. Pepsin is familiar to all of us. Molds also develop organic enzymes. As a rule they cause putrefaction. Bacteria contain enzymes. The study of molds, yeasts, and bacteria from the enzyme viewpoint is rapidly becoming a matter of commercial importance in the production of organic compounds.

Lactase, in one series of experiments, hydrolyzed lactose nearly 1,000 times as rapidly as did 2 N HCl.

Many, perhaps all, enzymes are activated by specific inorganic ions. Pepsin works at its best in 0.2 per cent acid (HCl of the stomach) and amylase of the pancreatic juice needs traces of chlorides and phosphates. Such activating ions are called co-enzymes.

TABLE OF ENZYMES
(Partial)

ENZYME	SUBSTANCE ACTED UPON	PRODUCT
Lipase......	Fats	Fatty acids and glycerol
Amylase ...	Starch and dextrins	Dextrins and maltose
Inulase	Inulin	Fructose
Sucrase (Invertase)	Sucrose	Glucose and fructose
Maltase	Maltose	Glucose
Lactase.....	Lactose	Glucose and galactose
Rennin.....	Casein	Paracasein
Pepsin	Proteins	Proteoses, peptones
Trypsin	Proteins, albumoses, peptones, peptides	Peptides, amino acids
Urease	Urea	Carbon dioxide and ammonia
Zymase.....	Glucose, fructose, mannose, galactose	Alcohol (ethanol) and carbon dioxide
Glycolase...	Hexose sugars	Lactic acid

Bacteria as Chemists.—Bacteria are the simplest forms of plants with such marvellous ability to multiply by cell-division that a single cell of some species can form more than 16,000,000 similar organism in twenty-four hours. Each bacterium is a mass of colloidal protoplasmic material surrounded by a thin semi-permeable wall. So small are they (some of them beyond the power of the microscope to see) that their surfaces, relative to mass, are enormous, and consequently the speed with which they manufacture toxins or harmless products, as the case may be, is apalling.

Dangerous though many species of bacteria are, yet many others are essential to higher animal and plant life. In the ruminant animals (cattle, etc.) intestinal bacteria attack cellulose but bacteria in the human intestine cannot do this. They obtain their energy from carbohydrates or proteins of our food, not from fats. Bacterial attack on carbohydrates produces non-toxic products such as lactic acid, butyric acid, alcohols, carbon dioxide, hydrogen, and methane.

The tremendous intestinal population in the human intestine, encouraged by the favorable slightly alkaline reaction of the lower section, attack the protein material or amino-acids there with formation of toxins. It is on this action that "auto-intoxication" is blamed. Bacterial action in the lower intestine is generally considered an unmixed curse to humanity. From the protein material may be formed toxic amines, phenols, carbon dioxide, hydrogen sulfide, ammonia, and fatty acids. These poisons may bring about actual illness and eventual senility.

A. I. Kendall states that the chemical action of bacteria depends in great measure upon the surrounding medium. If plenty of carbohydrates manage to reach the lower intestine (not easy to manage) the putrefying bacteria may get their energy from this food instead of from protein with the great advantage that harmless chemical products result.

For example, diphtheria bacilli attack intestinal amino-acids of protein with formation of the dangerous diphtheria toxins. Yet if plenty of lactose (with sugar) is present these bacteria will derive their energy from the lactose with formation of harmless products. Lactose is digested slowly enough that with the feeding of large quantities a part reaches the lower intestine.

The *bacillus acidophilus* (not Metchnikoff's sour milk *bacillus bulgaricus*) thrives upon carbohydrates but is totally unable to utilize protein material as a source of energy.

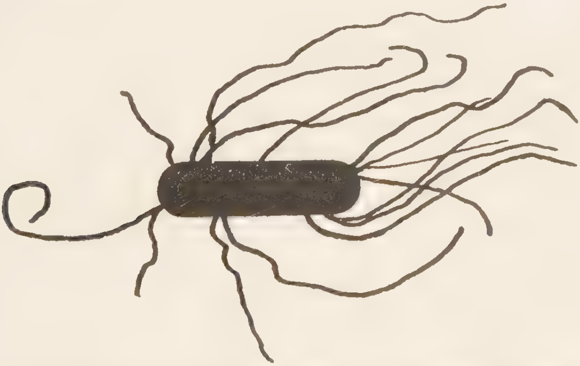
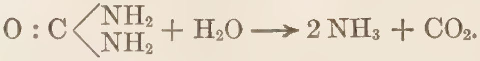


Fig. 122.—Chlostridium acetobutylicum which ferments corn starch to butyl alcohol, acetone, and hydrogen. 6,000 × natural size.

Chemists are now studying the chemistry of bacteria themselves with promising results. Not only may we learn more about immunity from disease, but we may compel bacteria to run large chemical factories for us. Of course we have always allowed the nitrifying bacteria on the roots of clover, alfalfa, and other legumes to convert the free nitrogen of the air into invaluable plant food, nitrites, nitrates, and ammonia.

Butyl alcohol is now being produced on a large scale (for the cellulose lacquer industry) by the friendly coöperation of *clostridium acetobutylicum* which converts starch into butanol, acetone, ethanol, hydrogen, and other products. Other microörganisms are now being put to work. The fungus, Aspergillus niger, makes citric acid out of sucrose. Other molds convert various sugars into oxalic, malic, and gluconic acids. Read page 327 for the action of yeasts.

Enzymes act upon astonishing amounts of material. Sucrose converts 200,000 times its own weight of sucrose. Urease, an enzyme of the globulin class, hydrolyzes urea so fast at 20° C. that it produces 120 times its own weight of ammonia every five minutes.



$$O:C\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right. + H_2O \longrightarrow 2\,NH_3 + CO_2.$$

Urease is (so far) the only enzyme ever isolated in pure, crystalline form, and it required nine years of effort by Sumner[1] to accomplish the task. Even so, there is some dispute over the purity of his urease.

EXERCISES

1. By what steps could you change starch into acetic acid? And on into acetone? Could you change cellulose into acetone?

2. Ten grams of a carbohydrate give, on complete combustion in air, 15.43 g. of carbon dioxide and 5.79 g. of water. What is its formula?

3. Assuming that 95 per cent of dextrose is converted into alcohol, what weight of dextrose would be required to prepare 100 g. of alcohol containing 95 per cent of C_2H_4OH by weight?

4. How many milligrams of invert sugar are present in each cubic centimeter of a solution prepared by inverting 3.42 g. of sucrose, and diluting the solution to one liter?

5. What are the products of the hydrolysis of (*a*) starch, (*b*) sucrose, (*c*) inulin? Compare the physical and chemical properties of starch and glucose.

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CHAPTER XXXII

CELLULOSE AND ITS ESTERS. RAYON

Cellulose.—Wood is, in general, made up of long fibers of cellulose $(C_6H_{10}O_5)_x$ cemented together by a gummy substance called lignin. In paper making this lignin is dissolved by digesting chips of the wood under pressure with a solution of calcium bisulfite, $Ca(HSO_3)_2$, or other reagents. The pulp of cellulose fibers is then shaken on a sieve through which the water drains and the fibers matted in a sort of "warp and woof" system. It is this interlacing that gives paper its strength. After passing through rolls to squeeze out the remaining water, a rosin size or glue size is spread over the surface to prevent undue spreading of ink. Usually the wet pulp is bleached and often dyed. Glazed papers that crack on creasing are loaded with clay, which gives body to the paper. The best writing paper may be made from linen rags. Cotton is nearly pure cellulose. The stringy part of vegetables is cellulose, but man makes little progress in digesting such fibers. The by-products of the cottonseed, once a nuisance, are worth $150,000,000 annually in this country alone.

It has been proved that wood pulp heated under pressure with dilute acids to convert cellulose into glucose yields much of a partially hydrolyzed cellulose suitable for stock food. This is a useful contribution to human welfare, since our pastures are no longer capable of supporting enough cattle for our needs. To utilize waste wood as a stock food will make possible more beef and cheaper beef.

Recently Bergius has overcome some of the technical difficulties and has hydrolyzed wood cellulose, by the aid of concentrated hydrochloric acid, to crude glucose, with good recovery of the concentrated acid. This process will help a country like Germany lacking enough native carbohydrate food but possessing plenty of wood waste. The simple sugars prepared from cellulose have been fermented by special bacteria to produce lactic acid (mixed with one tenth as much acetic acid) and with an 80–90 per cent yield.

Cellulose is dissolved by zinc chloride and the pasty mass molded into so-called "fiber buckets" and the like. They are light, strong, and can be given a waterproof surface.

Cellulose Nitrates.—When cellulose is attacked by concentrated nitric acid the hydroxyl groups of the cellulose unite with the hydrogen of the acid to form water. At the same time cellulose nitrate is formed. Concentrated sulfuric acid must be present to take up the water set free in the reaction.

$$(C_6H_{10}O_5)_2 + 6\ HNO_3 \longrightarrow C_{12}H_{14}(NO_3)_6 + 6\ H_2O.$$

When six nitrate groups are introduced a high explosive results, but with less vigorous nitration only three or four groups are introduced, forming the non-explosive pyroxylin, or "soluble cotton." Guncotton burns harmlessly, but is exploded by a detonating cap. When dissolved in acetone and some vaseline is added a liquid is obtained that dries to a tough horny mass, called smokeless powder. In practice the pasty mass is forced through dies so that the dried solid is perforated by small holes. On burning in the gun the surface increases and the force of explosion is not all exerted in one shattering instant but gathers strength as it progresses. In modern warfare all guns are fired with smokeless powder.

It is not to be thought that such manufacture is merely a deadly art. Without powerful explosives in great quantities there would be fewer railroad tunnels, no Panama Canal, less coal mined, less of most minerals secured, and no loosening of the hardpan where fruit trees are to be planted. Nor would so much land be cleared of stumps.

More than 30,000 men slaved eleven years to dig a three-mile tunnel for a Roman aqueduct. Thanks mainly to explosives the same tunnel could be built today by 100 men in 10 months.

The raw material for nitration is cotton linters (short fibers removed from cottonseed) but it is possible to nitrate very thin sheets of pure wood cellulose paper. The cellulose nitrate (wrongly called "nitro-cotton") used as a high explosive contains 12.4 to 13 per cent nitrogen.

"In the nitrocellulose industries to-day material of widely varying nitrogen content and solubility is used, ranging from 10.7 per cent to 13.5 per cent. The degree of nitration is the essential difference between the many varieties and determines largely the solubility in the various solvents. The lower forms of nitrocellulose from 10.7 per cent to 11.2 per cent nitrogen are utilized with camphor, triphenyl phosphate, and tricresyl phosphate to produce the well known celluloid plastics. This type is soluble in alcohol. That containing 11.2 per cent to 11.7 per cent nitrogen finds use in photographic films, alcohol soluble nitrocotton lacquers, and artificial silk. This type is completely soluble in ether-alcohol mixtures, wood alcohol, ethyl acetate, acetone, etc.

"Pyroxylin, or as it is generally called in the industry, soluble cotton, is the basis of lacquers. It has a nitrogen content of 11.8 per cent to 12.3 per cent and is readily soluble in all the common ester solvents, such as ethyl, butyl, and amyl acetate, methyl alcohol, and acetone. It is practically insoluble in alcohol but very soluble in alcohol-ether mixtures. Artificial leather is also produced from this type of nitro-cellulose. In making such auto finishes as "Duco," pyroxylin is heated with mildly alkaline agents to reduce the viscosity of the lacquer so it can be sprayed properly.

"Nitrocellulose of nitrogen content approximating 13.0 per cent forms the basis for smokeless powder and explosives. Types of such high degrees of nitration are not soluble in the usual solvents, but are soluble in acetone." (J. B. Wiesel.)

Nitroglycerine dissolves certain types of nitro-cotton to form a jelly, gelatin dynamite, much used in mining. With addition of ammonium nitrate the "ammonia dynamite" suitable for rock blasting is prepared. Common ***dynamite*** is usually a mixture of nitroglycerine, wood meal, and sodium nitrate. Ethylene glycol dinitrate is added to lower the freezing point of the nitroglycerine to the safety limit.

Pyroxylin and Celluloid Films.—The pyroxylin (lower nitrated cellulose) mentioned above dissolves in a mixture of alcohol and ether to form collodion. When this is poured on a cut the solvent evaporates and leaves a smooth transparent film of the pyroxylin. Dissolved in amyl acetate ("banana oil"), it forms an excellent waterproof lacquer for protecting metals. If castor oil is added, a flexible film results on drying. To prepare patent leather such a mixture containing lampblack or some color pigment is painted repeatedly on the leather.

Celluloid is prepared by mixing pyroxylin with camphor and a little alcohol and passing through heavy rolls. This transparent material is the basis of photo films, motion picture films, celluloid toilet articles, and other useful objects. Colored material may be stirred in when desired.

Synthetic camphor, made chiefly in Germany, from turpentine, is the only rival to the Japanese monopoly, forcing a price drop from \$3.40 per pound to \$0.90 in a single year. It is useful in keeping the price down to a reasonable level. Camphor is indispensable in the manufacture of pyroxylin plastics such as celluloid (movie film, etc.).

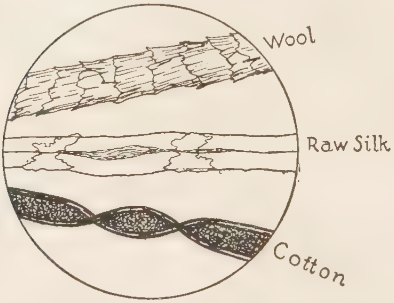

Fig. 123.—Highly magnified fibers of wool, raw silk and cotton.

Artificial leather, although not so strong as the natural product, is handsome and useful. A canvas foundation is coated with a colored pyroxylin solution containing certain oils to make it flexible. After rolling, it is embossed by other rolls that have the desired design engraved on their surface.

In fact the number of excellent and useful imitations of established products made possible by a clever use of pyroxylin solutions is astonishing. Among these are various expensive furs from cheaper ones, damask, eider down cloaks, brocade, carpets, and artificial silk.

The automobile lacquers (Duco, etc.) contain cellulose nitrate (11.8 to 12.3 per cent nitrogen), resins, pigments, solvents, diluents, and plasticizers or softeners. Among the solvents are ethyl, butyl and amyl acetates, methyl alcohol, and acetone. Glycol ethers have lately been added to this list.

The plastizers which soften and give elasticity to the film, include dibutyl phthalate, tricresyl phosphate, and oxidized castor oil.

Cellulose Acetate.—Cellulose, as already shown, reacts like an alcohol with acids or acid anhydrides because of its hydroxyl groups. With acetic anhydride it forms the useful ester called cellulose acetate. Worked into movie films by the aid of camphor, it forms a product similar to the usual celluloid film but only slightly inflammable. If it can be made as flexible and permanent, it should displace the dangerous celluloid film. The initial cost is greater because acetic anhydride costs more than nitric acid yet with its use fireproof booths and insurance costs would disappear. There is, furthermore, good indication that acetic anhydride will soon be produced much more cheaply.

Cellulose acetate silk finds a growing demand because it stands washing better than any other rayon type.

Rayon.—Manufacturers insist on use of the word *"rayon"* instead of "artificial silk" or "imitation silk." There are three types in large use—cellulose nitrate, cellulose acetate, and viscose.

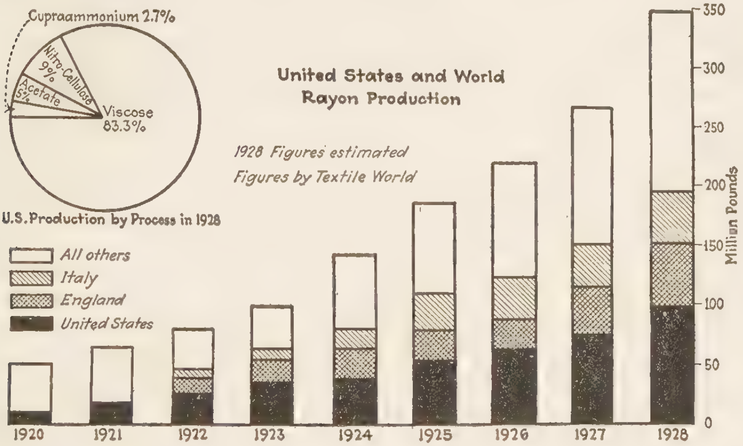

FIG. 124.

To make rayon from cellulose nitrate, pyroxylin solution is forced through fine dies or capillary tubes, and the threads, drying as they form, are denitrated in a bath. They are then spun into "silk" threads. Silk is a protein, but these denitrated fibers are restored to their original condition as cellulose, or cotton, but with an astonishing change in appearance and properties. In luster they are even more brilliant than silk, taking dyes with great beauty of effect. The synthetic silk industry, not depending on this process alone, is of some magnitude, the world's output reaching a total of 400,000,000 pounds in 1929. The United States leads with 130,000,000 pounds and an astonishing annual increase in production, over 30 per cent at present.

Cellulose acetate silk is simply spun without any treatment comparable to denitration. The ester itself is only slightly inflammable so remains as the ester in the finished silk.

Viscose silk is made from wood cellulose by treatment with sodium hydroxide and carbon disulfide, forming first a yellow soluble compound called cellulose xanthate. This is aged, then spun into threads, and decomposed by acid back into the original cellulose, but with the silken luster desired. Viscose at present leads all other silks with more than 80 per cent of the total. It is less durable than natural silk, but of course is far cheaper.

Although the world use of natural silk has increased somewhat, it is exceeded by the various rayons. This simply means that many people who could not afford real silk now can buy the cheaper but equally lustrous rayon.

Farm Wastes.—There are annually produced 150,000,000 tons of corn stalks in the United States and 20,000,000 tons of corn cobs. The cellulose of the stalks can be made into good paper, in fact one mill began commercial production in 1928.

Furfural is now being made from oat husks and can be made from corn cobs. Several chemical products are possible from stalks, straw, and other cellulose-rich farm material.

EXERCISES

1. What difference would it make to you if cellulose could not be nitrated?
2. What would happen to the pyroxylin type of cellulose nitrate if the excess of nitric acid used in nitration was not carefully washed out?

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CHAPTER XXXIII

FOOD AND NUTRITION

Food is needed by the animal body to replace worn-out tissues, provide for growth in the young, and supply heat to maintain the body temperature. Of course food is the source of all the bodily energy. When a muscle contracts tissue is oxidized and heat liberated. It has been definitely proved that the body is a very efficient sort of an engine. The same amount of energy in the ultimate form of heat is liberated when we eat and digest food enough to produce, say, 100 grams of carbon dioxide in the exhaled air as when enough coal is burned under a boiler to produce 100 grams of carbon dioxide. The average adult exhales 1100 grams of carbon dioxide, excretes 25 grams of urea, and large quantities of hydrogen and oxygen in the form of water, daily. Protein is finally burned to urea while starch, sugar, and fats are burned to carbon dioxide and water. An alcohol lamp burning a pint a day is as large a source of heat or other energy, as an average man.

Classification of Foods.—In addition to water and air, the human body requires food from four great classes.

Protein we get in lean meat, milk, cheese, eggs, beans, peas, and the cereals. The protein molecule is very large and very complex, and has a probable molecular weight of several thousand. Protein is essentially a nitrogen food, but it also contains carbon, hydrogen, oxygen, and sulfur.

Different proteins are built up from seventeen different amino acids (organic acids containing the NH_2 group) and although some of these acids may be synthesized from others in the body, others are essential. Cystine, the only amino acid containing sulfur, is essential to life and lysine to growth. So proteins lacking such amino acids are incomplete and must be balanced in the diet by other proteins. White bread lacks lysine unless considerable milk is added in the baking as is now done with the best of the commercial breads.

Fats are found in meat, milk, nuts, and the oils expressed from corn, cottonseed, peanuts, coconuts, and soya beans.

Carbohydrates are found as starch in the cereals, in rice, potatoes chestnuts, and various tubers and as sugars in cane, beets, fruits, and other products.

Mineral salts, or compounds, particularly those of iron, calcium, phosphorus, and iodine are obtained from milk, eggs, legumes, vegetables, meats, and whole grains.

In listing food requirements it is important not to overlook the vitamins so necessary to growth and vigor, or the cellulose roughage needed to give bulk and to keep the digestive material moving along.

Digestion.—It is a strange fact that animals are unable to assimilate the very simple foods that nourish plants. And yet the carbon dioxide, nitrates, ammonia, and potassium salts so relished by plants are soluble, while with the exception of sugars, food for animals is insoluble and must be made soluble by the process of digestion before it can be transported throughout the body tissues.

- Protein
  - Partly broken down in the stomach by ***pepsin.***
  - Completely torn apart in small intestine by ***trypsin*** and ***erepsin.***
  - Products carried through intestinal wall to all parts of body.
  - Products built up again into muscle.
- Fats
  - Emulsified into minute droplets by ***bile*** in the small intestine.
  - Split by ***lipase*** into fatty acids and glycerine.
  - Products pass through intestinal wall.
  - Transported and built into fats again.
  - Oxidized as a fuel for energy.
- Carbohydrates
  - Starch partly digested by ***ptyalin*** of saliva.
  - Starch converted (by ***amylase*** of intestine) into malt sugar (maltose).
  - Maltose → glucose (by ***maltase***).
  - Glucose passes through intestinal wall.
  - Glucose oxidized as fuel for energy.
  - Cane sugar split by ***sucrase*** of the intestine into glucose and fructose.

In the outline above, the enzymes of the digestive fluids are printed in heavy type. It is not essential that you commit their names to memory, but you should know something of the general processes of digestion.

As much as 58 per cent of the total protein may be converted into carbohydrate in the body but this is wasteful and taxing. The final end of protein nitrogen is urea, excreted in the urine.

Monosaccharides are absorbed into the blood and in the liver converted into a starch-like substance called glycogen. Glycogen is decomposed into dextrose as needed, the dextrose ending as carbon dioxide and water with release of energy. It seems that the fatty acids and some amino acids are best oxidized when glucose is simultaneously oxidized.

Fats can be converted by the animal body into carbohydrates and carbohydrates into fats.

The Fuel Value of Food.—One gram of fat burned in the body yields 9 Cal. (1 Cal. = 1000 cal.), and it yields but little more when actually burned with flame in a calorimeter. From the analysis of any given food one can readily compute the energy value of a pound or kilo of that food. The fuel values given here are, perhaps, a trifle too low.

$$\text{Fuel values}\begin{cases}1\text{ g. fat} = 9\text{ Cal.}\\ 1\text{ g. protein} = 4\text{ Cal.}\\ 1\text{ g. carbohydrate} = 4\text{ Cal.}\end{cases}$$

The Balanced Ration.—A man engaged in moderately active muscular work should obtain from his food about 3500 Calories of energy, 80 grams of protein, 0.68 gram of calcium, and 1.32 grams of phosphorus and 0.015 gram of iron. However, this energy demand varies with the weight of the individual and with the amount of exercise taken. A man of average weight living indoors with but little exertion requires only 2200 Calories a day, and a woman only 1760 Calories. A growing youth requires more.

It would be possible, but very painful, to get all of this energy from butter or from sugar, two of our most highly concentrated foods. A study of food charts and pocketbooks may lead to an undue enthusiasm for oatmeal or dried beans; but most digestions would soon rebel. Common sense must be used in selecting foods.

A varied diet, stressing milk and fresh vegetables, is the best. The utilization of fats is greatly aided by carbohydrates. More starch can be tolerated than sugar.

White bread is far from being a complete food, but recently there has come on the market a commercial loaf enriched by a good deal of milk or powdered milk and by the salts and vitamins extracted from bran and the wheat grain. This milk bread comes nearer the balanced ration than any previously sold.

The mineral salts, which it seems unwise to leave to chance, are compounds of iron, calcium, phosphorus, and iodine.

Iron, essential to the red hæmoglobin of the blood and to cell nuclei, is found in unusual quantities in egg yolk, spinach, beans, whole-wheat bread, oatmeal, beef, raisins, cholocate, and oysters.

Calcium, essential to the bones, is secured from milk, cheese, oatmeal, whole-wheat bread, oysters, beans, eggs, chocolate, walnuts, fruits, and vegetables.

Phosphorus, also essential to the bones, and to every cell as well, is furnished by milk, cheese, eggs, chocolate, walnuts, beef, fruits, and vegetables.

It is now suspected that traces of copper may catalyze the production of the red hæmoglobin of the blood. Pernicious anemia results from a deficiency of hæmoglobin.

The ash, or mineral part of the food, is absorbed into the blood after digestion. In health the blood is faintly basic or alkaline and should not have this condition disturbed by excessive use of acid-forming foods. In general the ash of white bread, meat, eggs, and rice is acid while the ash of milk, vegetables, and fruits is basic. Here is another reason for the extensive use of a milk and vegetable diet.

The merits of variety in diet are evident when we learn the composition of foods not in daily use. For example, a study of food analyses leads us to an appreciation of the extraordinary value of oysters as a source of sodium iodide, iron, calcium, and phosphorus. Walnuts have similar value except for iodides. Yet after all precautions are taken to secure the right number of calories, adequate protein, and sufficient calcium, iron, phosphorus, roughage sodium chloride, and even the little sodium iodide needed to prevent goiter, the patient may waste away for lack of vitamins.

Vitamins.—A deficiency disease called scurvy has been known for centuries, but it is only recently that we have gained full knowledge of it. Vasco da Gama, Captain Cook, and other ancient mariners on long voyages lost many men from this scourge, as did also armies in the field. At last it was found that lemon juice cured scurvy. Parts of China, where the poor lived mainly on polished rice, were afflicted with beriberi, another deficiency disease. When scientists added these polishings—the outer part of the grain—to the diet, the Chinese recovered.

These and similar observations led to the discovery that animals require for growth and health very small quantities of certain accessory food substances not recognized by analysis of animal tissues. These accessories, unheard of before 1911, we call vitamins. They are difficult to prepare, and their chemistry is not yet well understood. Four are well known, and at least two more have recently been announced.

"Unless at least a pint of milk a day per person is used in a community, serious nutritional errors are certain to develop and affect the vitality, sturdiness, and capacity to resist disease of a large number of both children and adults."—Prof. Henry C. Sherman, Columbia University.

Vitamin A (Fat-soluble A). Vitamin A merits special attention because many of our staple foods are poor in it and because a diet deficient in this vitamin lowers resistance to infectious diseases. Without it young animals do not grow properly. Sherman insists that in order to keep the body up to its maximum vigor and efficiency much more of A is required than is needed to maintain normal growth.

Diets composed essentially of bread, meat, potatoes, sugar, and fats other than butter are likely to contain too little of Vitamin A. Unfortunately such diets are all too common. For that matter, such a diet is deficient in the other vitamins and in salts; so it may well be considered unsafe.

The richest sources of A are butter and all milk products, cod liver oil, eggs, green leafy vegetables, tomatoes, and green peas. A very concentrated extract of this vitamin was prepared from cod liver oil, 10,000 pounds yielding 1 pound. Oleomargarine or nutmargarine with a trace of this potent extract added would come nearer to equalling real butter as a food. Rancid fats lose all their Vitamin A content.

Vitamin B. Any varied diet contains a plentiful supply of Vitamin B. Nevertheless, the growing tendency to give highly refined foods a leading place on the table makes a deficiency possible.

This is the vitamin that cures beriberi, a nerve disease. The use of food poor in Vitamin B often results in serious impairment of appetite, digestion, and general vigor. Consequently it is well to have considerably more of it than the amount needed to prevent beriberi and to sustain normal growth (Sherman).

Dried yeast seems to be a richer source of B than any of the cereal grains, even wheat and barley. Drummond reports that young animals need more Vitamin B than adults and that the first symptom of deficiency is loss of appetite which leads to loss of weight. In such cases the eating of dried yeast cakes may be something better than a popular fad. Vitamin B is the most stable of all the vitamins toward cooking and oxidation.

Vitamin B seems to have a greater influence on lactation than has E.

There is good evidence for the existence of a ***Vitamin G*** (the more heat-stable part of B) which is essential to the health of skin and hair, and may really be the pellagra-preventative part of Vitamin B. Brewer's dried yeast is one of the rich sources. Other good sources are eggs, milk, tomatoes, and carrots.

Vitamin C. Vitamin C protects from scurvy and increases resistance to infectious diseases. There is much more danger of an insufficient intake of C than of B, and it merits attention. Fruits, green peas, and tomatoes (fresh or canned) are especially rich in Vitamin C. It is rather easily destroyed by cooking, unless the food is acid, as is the case with canned tomatoes. Children on a pasteurized milk diet need orange juice or tomato juice to prevent scurvy and to promote growth. It has recently been proved, too, that canned peas are about as rich in Vitamin C as are canned tomatoes.

Exclusion of air during cooking by the canner gives him an advantage over the home cooker in preserving Vitamin C.

Vitamin D. Vitamin D prevents or cures rickets, a poor bone development in children. No doubt it enables the proper tissues to take up calcium salts from the blood stream. Since rickets, in some degree, troubles a very considerable fraction of the nation's children, its cure or prevention is a matter of vital importance. Cod liver oil is the best source for D as for A but fortunately it has been shown in 1927–28 that, by the action of ultra-violet light of sun or special lamp, ergosterol is converted to some substance (perhaps Vitamin D) that cures rickets. Ergosterol is found in traces in the non-saponifiable portion of some food fats, perhaps in other portions. The commercial irradiation of foods has just begun.

Already poultry raisers are irradiating their birds with ultra-violet light with excellent results and cod liver oil by the carload is mixed with poultry food. Doctors now treat children on cloudy winter days with ultra-violet light from suitable lamps and the results justify the treatment.

Food Sources of Vitamins A, B, and C

	"A"	"B"	"C"
Milk, fresh (unpasteurized)	+++	++	++
" dried (whole milk)	+++	++	+
Cream	+++	++	++
Butter	+++	—	—
Cheese	++	++	—
Spinach (fresh)	+++	+++	+++
" (canned)	+++	+	+++
Eggs	+++	++	—
Tomatoes (fresh or canned)	++	+++	+++
Cabbage (raw)	++	++	+++
" (cooked 20 minutes)	++	++	++
Lettuce (green)	++	++	+++
Peas (fresh)	++	++	++
Oranges	+	++	+++
Lemons	—	++	+++
Berries	—	—	+++
Peaches (raw or canned)	++	+	++
Apples	+	++	+
Grapefruit	?	++	++
Grape juice	?	+	+
Beans (fresh string)	++	++	++
Beans (navy)	+	+++	—
Potatoes	+	++	++
Carrots	+++	+	+
Turnips	+	++	+++
Liver	++	++	?
Nuts	?	++	?
Onions	?	++	++
Squash	++	+	?
Peppers (green)	+++	++	+++
Turnip greens	+	+++	+

+ Contains the Vitamin.
++ Good source of the Vitamin.
+++ Excellent source of the Vitamin.
— Lacks the Vitamin.
? Uncertain.

Note: The only foods that are excellent or good sources of all three leading vitamins are milk, spinach, tomatoes, cabbage, lettuce, green peppers and peas. Canned peas still retain a good amount of the vitamins. Cod liver oil is remarkably rich in Vitamins A and D but is hardly to be classed as a food. Prunes are thought to be rich in B and G. Other good sources of Vitamin G are milk, tomatoes and carrots.

Of course, ignorant or careless use of ultra-violet light may cause serious sunburn or eye trouble. A physician's advice is desirable. Vitamin D is not destroyed by cooking, exposure to air, or by moisture.

Vitamin E. This vitamin, found in wheat germs and oils extracted from grains and to a slight extent in butter, has a profound influence on reproduction and on lactation of mothers. It seems to be rather stable.

There is a tendency now to consider the possible existence of two vitamins equivalent to E just as B probably represents a group.

In general it is safe practice to eat an abundance of milk and fresh vegetables. Spinach, lettuce, cabbage, tomatoes, carrots, onions, peas, and fresh string beans are invaluable for their vitamin content. Now it is easy to believe that a sandwich made of milk bread, a little butter, and a lettuce leaf meets many of our food requirements.

The identification of vitamins in foods is tedious, involving for each vitamin the feeding of white rats or other test animals with a diet free from the vitamin in question until the animals are definitely sick or losing weight. Then the food or food extract to be tested is fed and growth and general health observed. Carr and Price[1] discovered a color test for Vitamin A, using antimony trichloride in chloroform. Although its infallibility is questioned by a few, this test has been widely accepted. Its use greatly

VITAMIN INFLUENCES

Vitamin A	Aids growth, general health and resistance to disease. Prevents certain eye infections, indirectly.
Vitamin B	Prevents beriberi in man and polyneuritis in birds.
Vitamin C	Prevents scurvy.
Vitamin D	Prevents rickets.
Vitamin E	Aids reproduction and lactation.
Vitamin G	Prevents pellagra in man. Probably keeps skin and hair healthy in animals.

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[1] *Biochemical Journal, 21*, 497, 1926.

expedites vitamin testing of foods and vitamin research. We desperately need quick and reliable color tests for the other vitamins.

Prolonged boiling of vegetables in excessive volumes of water and draining off this water is to blame for a great *loss of valuable mineral salts.* Cooking by steaming might save this loss and the use of a minimum of water would help.

Chart of Foods (Ready to Serve)

Food	Protein, Per Cent	Fat, Per Cent	Carbo-hydrates, Per Cent	Helping in Grams	Total Calories
Bread (white)	9.1	1.6	53.3	85	230.0
Butter	1.0	85.0		21	169.0
Beef (lean round)	19.0	13.0		128	250.0
Bacon (smoked)	10.5	66.0		28	188.6
Beans (fresh string)	17.0	15	5.0	113	48.7
Beans (baked canned)	9.6	5.5	3.3	184	364.0
Chicken (fricasseed)	17.7	11.4	2.3	100	187.0
Eggs (two)	13.4	10.5		106	179.0
Fish (whitefish)	18.7	5.3		128	160.0
Lamb chops (broiled)	21.7	29.9		57	210.0
Lettuce	1.2	0.3	2.9	28	7.0
French dressing		75		17	115.0
Milk	3.3	4.0	5.0	170	123.6
Oatmeal	2.8	0.5	11.5	196	121
Cream for oatmeal	2.5	18.5	4.5	96	186.0
Sugar			100.0	21	81.0
Potato (baked)	3.3	0.3	22.7	210	245.0
Orange	0.8	0.2	11.6	141	75.0
Peas (green)	4.3	3.3	6.7	100	121.0
Pie (apple)	6.5	6.9	32.0	127	283.0
Rice	2.8		24	162	180.0

EXERCISES

1. From the above chart make out a menu for the three meals of the day, tabulating the weight in grams of each portion as near as can be estimated, the percentage of fat, protein, and carbohydrate and the total fuel value of each portion. The total for the day must be 2500 Cal. and about 80 g. of protein must be included. The calculations must be based upon the analyses given in the table. More extensive tables are found in books by Sherman and Eddy given in the following list of references. In Rose's *Feeding the Family* may be found a table giving the weight of 100-calorie portions of various foods and another giving calories per pound.
2. How can we test a food for vitamins?
3. Why is not one protein as good as another?

4. What is an enzyme? Have you any with you?
5. Name five foods that are rich in all three vitamins.
6. What are the best food sources of calcium, phosphorus, and iron?
7. What finally becomes of the protein nitrogen in the body?
8. Give the weights of carbohydrate, protein, and fat which would supply a menu, such that the total food value was 3000 Cal., that 80 g. of protein was included, and that the remaining fuel value was divided equally between carbohydrates and fats.

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CHAPTER XXXIV

SILICON AND BORON

allotropic.

Silicon and boron exist in both crystalline and amorphous forms. When hot aluminum is used to reduce the oxides of these elements, the liberated silicon (or boron) dissolves in the excess of melted aluminum from which it crystallizes on cooling. If the oxides are reduced in some non-solvent medium only amorphous forms of the elements are obtained. However, these amorphous elements may be dissolved in molten aluminum and obtained as crystals on cooling. Distillation of either form yields the crystalline form as the condensate. X-ray studies indicate that amorphous silicon and boron differ from the crystalline not in crystal lattice but only in size of particle.

SILICON

Silicon resembles carbon in its valence of four and in the weakly acid properties of its hydroxide. It also forms a series of compounds remarkably like the compounds of carbon. For example, SiH_4 is comparable to CH_4; $SiCl_4$ to CCl_4; and $SiHCl_3$ (silicochloroform) to $CHCl_3$ (chloroform). There are many more such compounds of silicon, but they differ from carbon compounds in that silicon atoms will not link up with each other in large molecules as do carbon atoms. The limit in stability of such chain compounds is represented by Si_6H_{14}.

Occurrence.—Silicon does not occur free but it is the commonest element after oxygen. Over one-fourth the earth's crust is combined silicon. Its oxide (SiO_2) is found everywhere as quartz or in sand and sandstone. Clay and all common rocks except limestone and dolomite are silicates. Silicon is the central element of the mineral world much as carbon is in the plant and animal realm.

Preparation.—Silicon was first made by Berzelius in 1823 by heating potassium with silicon tetrachloride. There are at least four reducing agents effective in the preparation of silicon as shown by the following equations:

$$\begin{aligned} SiCl_4 + 4\,K &\longrightarrow 4\,KCl + Si, \\ SiO_2 + 2\,Mg &\longrightarrow 2\,MgO + Si, \\ 3\,SiO_2 + 4\,Al &\longrightarrow 2\,Al_2O_3 + 3\,Si, \\ SiO_2 + 2\,C &\longrightarrow 2\,CO + Si. \end{aligned}$$

The preparation of the element by reduction of the oxide is not easy. However, carbon reduces the oxide at the high temperature of the electric furnace and large quantities are now made that way. The process resembles the manufacture of carborundum except that less coke is used. When a mixture of iron oxide and silicon dioxide is reduced with carbon, ferrosilicon is produced. It is much used in steel making to remove air bubbles. The hot silicon unites with oxygen. An iron alloy containing 14 per cent silicon, known as duriron, is used for condensers in nitric acid plants because of its remarkable resistance to the attack of acid. This alloy is very hard and brittle.

Silicon steel, containing only a few per cent of silicon, has for the past eighteen years been used for transformer cores and in that time has saved the electrical industry hundreds of millions of dollars. With the previous iron cores there was a considerable heat loss when the magnetic state of the transformer was changed. This and other losses were greatly reduced by silicon steel. Under low magnetizing forces it is far more magnetic than the best Swedish iron and this quality does not deteriorate.

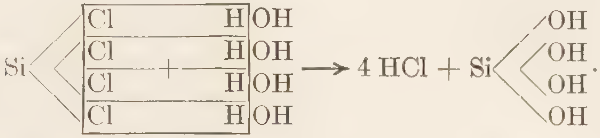
Properties.—Amorphous silicon is a brown powder, while the crystalline form is obtained in hard, black, hexagonal needles. The element is readily attacked by the halogens, forming gases. At high temperatures it forms silicides like CSi. Silicon displaces hydrogen from hot solutions of sodium hydroxide thus making possible a convenient military method of making hydrogen for balloons:

$$4\,NaOH + Si \longrightarrow Na_4SiO_4 + 2\,H_2.$$

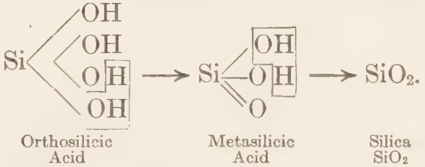
Silicon Tetrachloride, $SiCl_4$.—This colorless liquid boiling at 59° is made by direct union of silicon and chlorine at 430°:

$$Si + 2\,Cl_2 \longrightarrow SiCl_4.$$

It used to be prepared by the combined attack of hot carbon and chlorine on silicon dioxide, the carbon pulling at the oxygen and the chlorine at the silicon. The liquid fumes badly in moist air and so was used to some extent in producing smoke screens for military purposes. Water hydrolyzes it completely, forming orthosilicic acid. Compare this with the hydrolysis of the chlorides of phosphorus:



The Silicic Acids.—Orthosilicic acid is prepared by hydrolysis of the chloride or decomposition of silicates with acids. It is such an extremely weak acid that its ammonium salt has never been isolated, due to its complete hydrolysis. By progressive dehydration orthosilicic acid is finally converted into its anhydride, silica (SiO_2). The loss of water is facilitated by heating.



A convenient laboratory method of preparing silicic acid is to acidify a soluble silicate such as "water glass" (Na_2SiO_3):

$$Na_2SiO_3 + 2\,HCl \longrightarrow 2\,NaCl + H_2SiO_3.$$

A water glass solution of 1.16 sp. gr. may be added to approximately 8 per cent hydrochloric acid. With proper precautions the entire mass turns into solid jelly, more water being held by the silica than is called for by the formula. This jelly may be washed, and then dried in the oven to a fine powder (SiO_2). In the following chapter there is more about silicic acid.

Silica, SiO_2.—Quartz or silica is one of the common minerals. It crystallizes in six-sided prisms as rock crystal.

Sand is partly disintegrated quartz and when the grains are cemented together with silica or lime under nature's pressure, sandstone results. Iron oxide impurities often give it color. In smoky cities sandstone with a lime cement is disintegrated by the acid nature of the smoke.

Above 875° quartz is slowly converted into rhombic crystals with a density of 2.2, while below that temperature the hexagonal crystals with a density of 2.0 are stable. Quartz melts at 1700°–1800°, but it is difficult to observe any sharp melting point. It softens gradually, due to its great viscosity even when fluid. It boils at 2230° and part of the vapor condenses as trydimite.

As the anhydride of an acid it reacts with bases but not with acids (except hydrofluoric acid). With fused sodium carbonate it displaces carbon dioxide, as would any ordinary acid. The volatility of one of the products, carbon dioxide, prevents reversal of the reaction:

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2.$$

Silica reacts with hydrofluoric acid with formation of the gas silicon tetrafluoride:

$$SiO_2 + 2\,H_2F_2 \longrightarrow 2\,H_2O + SiF_4\uparrow.$$

Clear Fused Quartz.—E. R. Berry of the General Electric Company has recently prepared large blocks of clear fused quartz and given definite promise of an industrial future for this remarkable material.

By his process "rock crystal" fragments closely packed in a furnace are melted and given alternate vacuum and pressure treatment to get rid of air bubbles. So clear is the product that a rod one meter long transmits 93 per cent of the light entering at one end. Since its coefficient of expansion is only 7 per cent that of ordinary glass it can stand sudden changes of temperature without cracking. Its small increase in length with large change of temperature makes it suitable for clock pendulums, tuning forks, and thermometers, as well as for huge lenses and reflectors in astronomical instruments. The breaking of lenses in motion picture machines would be much less frequent if quartz lenses were used.

Since quartz is the best solid material for transmission of ultra-violet light it is desirable that hospitals should, in time, use quartz window panes so that patients may get the curative effect of the sun's ultra-violet rays. With cheapening of this material many applications will be found. There are now, however, some special glasses of value for such therapeutic purposes.

Water Glass.—Water glass may be made in two ways. Sand is boiled (under pressure) with a strong solution of sodium hydroxide, or sand is treated with fused sodium carbonate. In either case sodium metasilicate is formed:

$$SiO_2 + 2\,NaOH \longrightarrow Na_2SiO_3 + H_2O,$$
$$SiO_2 + Na_2CO_3 \longrightarrow Na_2SiO_3 + CO_2.$$

Water glass is sold in great quantities (400,000 tons annually) in the form of a concentrated solution, a thick syrup of about 1.38

specific gravity. When allowed to dry it forms a brittle, glassy solid. As a salt of a weak acid and a strong base (see Hydrolysis) its aqueous solution has a strongly basic reaction:

$$Na_2SiO_3 + 2\ H_2O \rightleftarrows 2\ NaOH + H_2SiO_3.$$

Of course free silicic acid must be present, yet we know it is insoluble. In a freshly diluted solution none can be seen. The explanation is found in the next chapter—the acid particles are too small to be seen and are spoken of as in colloidal suspension. On long standing these small particles of silicic acid aggregate and settle out as a visible precipitate.

The composition of water glass may be varied from $Na_2SiO_3 \cdot SiO_2$ to $Na_2SiO_3 \cdot 3\ SiO_2$ with resultant variation in properties.

Water glass has a variety of uses. It is the cheapest glue known. The heavy cardboard shipping boxes of to-day are built up from paper sheets glued together. Artificial stone is prepared from small lumps of stone and sand, with a water glass binder. Wood, cloth, and paper are fireproofed with water glass. It is a filler and binder in cheap soaps. One part of the common commercial syrup mixed with ten to fifteen parts of water, boiled to remove carbon dioxide, is an excellent egg preservative.

A trace of sodium silicate in collapsible aluminum tubes containing shaving cream or other alkaline pastes protects the metal from attack. It also checks corrosion of iron and lead water pipes when present in as little as five parts per million of soft water. Dust-proofing of concrete floors, surfacing some kinds of paper, and increasing the detergent value of many soaps are among the uses to which this cheap material is put.

Silicate Minerals.—Although it is difficult if not impossible to isolate definite silicic acids, salts of several different ones are found as minerals.

Orthosilicates (from H_4SiO_4)	Mica, $KH_2Al_3(SiO_4)_3$ Kaolin, $H_2Al_2(SiO_4)_2 \cdot H_2O$ Garnet, $Ca_3Al_2(SiO_4)_3$
Metasilicates (from H_2SiO_3)	Asbestos, $CaMg_3(SiO_3)_4$ Soapstone or talc, $Mg_3H_2(SiO_3)_4$ Beryl, $Gl_3Al_2(SiO_3)_6$
Disilicates (from $H_6Si_2O_7$)	Serpentine, $Mg_3Si_2O_7 \cdot 2\ H_2O$
Trisilicates (from $H_4Si_3O_8$)	Orthoclase; $KAlSi_3O_8$

In decomposing these silicates for analysis they are powdered and fused with sodium carbonate:

$$CaSiO_3 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SiO_3.$$

The silicates dissolve in melted soda, while carbonates do not, so the reaction is not reversible. On addition of hydrochloric acid everything dissolves. Evaporation of the residue dehydrates the silicic acid liberated from sodium silicate. This is finally weighed as pure silica. The soluble chloride of calcium (or other metal) is removed and determined by the usual methods.

Exercise 1.—Write the equations representing the action of hydrochloric acid on the fusion product just discussed.

Exercise 2.—How many grams of water glass can be made from 150 g. of pure sand? If fused with soda, how many liters of carbon dioxide would be released?

Glass.—Glass is a mixture of silicates, usually of sodium and calcium, although many variations are possible. Common glass might be considered as $Na_2SiO_3 \cdot CaSiO_3$, but in practice contains more silica. (Compare with water glass.) Window glass is usually $Na_2O \cdot CaO \cdot 6\,SiO_2$. This does not mean that Na_2O is actually present as such. The formula is merely a convenient representation of an analysis.

Glass making was one of the earliest arts. Glass beads were found in the tombs of the rulers of the First Egyptian Dynasty, 5000 B.C., and glass tear bottles were discovered in the tombs of later Pharaohs about 4700 B.C.

Glass is made by melting sand, lime, and soda in a gas-heated furnace. If iron is present as an impurity, the glass is green. This is the color of ferrous silicate. Since ferric silicate has a very weak yellow color it is an advantage to oxidize the green ferrous salt with manganese dioxide. Too much manganese introduces the amethyst of manganese silicate. Selenium is now replacing manganese dioxide as a color corrector. Soft, or low-melting, glass is of the lime-soda type. Hard glass, of higher melting point is prepared by substituting potassium carbonate for the sodium carbonate.

Window glass is blown from a ball into a cylinder, cut open while hot, and allowed to flatten in the annealing oven. Bottles are made by blowing the glass in a mold. Where window glass cylinders were formerly blown by the lung power of strong men, they are now blown by machines. A hollow ring is lowered into a batch of molten glass, a bubble started and then the ring is raised while air is blown into the bubble. As a result a beautiful glowing cylinder forty feet high and two feet wide is suspended in the dark factory like a pillar of light. This cylinder is lowered to supports, cut open, allowed to flatten and in general handled like the old six-foot cylinders.

Flat glass is now being drawn from a molten batch by an iron bar three inches wide and six feet long. This bar is attached to flexible metal strips so the slowly moving sheet can be run over bending rolls to the flattening table. It is finally cut into sheets and acid-cleaned.

The Owens bottle-blowing machine now does the work of fifty men, a single machine making 10,000 bottles per hour. It is evidently needed, for the United States uses twenty-five million gross of bottles yearly.

Plate glass is cast on a wide iron table, rolled flat, and, when cold, ground to remove unevenness and polished with rouge. In some factories the plate glass melt is allowed to flow on a revolving drum and is then passed under a roller, cut into sheets and annealed.

The automobile industry has created a demand for plate glass exceeding even that of show windows. The possibility of accident and injury from flying glass has led to the use of non-shattering glass windshields and windows. Two layers of sheet glass and a middle layer of celluloid with a suitable adhesive are powerfully compressed. Under impact the flexible center layer holds broken fragments. A similar laminated glass (five layers) is in use for bulletproof windows in bank offices. Such a glass one inch thick turns aside machine gun fire at 45 feet.

Flint glass is used for optical work and in making cut glass because of its high index of refraction. Lead oxide is here substituted for calcium oxide with addition of potassium nitrate to prevent reduction to metallic lead. Flint glass is "cut" on a grinding wheel into ornamental designs. When the pattern is deep the glass is molded, but the surfaces need polishing to make them smooth facets for the diamond-like sparkle desired. Dilute hydrofluoric acid is now used in polishing cut glass.

In 1927 the largest disk of optical glass ever cast in the United States was poured by the Bureau of Standards. It measured 70 inches in diameter and 12.5 inches in thickness, and so, if allowed to cool without restraint, would

SiO_2 [illegible]; rather difficult to get into solution

$CaSiO_3 + Na_2CO_3 \rightarrow Na_2SiO_3 + CaCO_3$

have been shattered by the great strains set up from the shrinkage of the rapidly cooling outside. This particular disk was carefully "annealed," allowed to cool for nine months at a rate regulated by proper insulation with sand and by heating devices. This mass of borosilicate glass weighed 3,500 lbs.

Resistance glass of the pyrex type contains some boron trioxide in place of part of the silica. It resists the attack of chemical reagents very well and is essential to the laboratory. Since it expands very little with heating it is not likely to crack with sudden temperature changes. This property with its unusual strength made pyrex glass very popular for baking dishes. During the war the Allies suffered for want of chemical glass formerly made in Austria and Germany. Necessity proved to be the mother of invention, for we now make chemical glass equal or superior to the best produced abroad. Cheaper borax will lower the cost of pyrex glassware and extend its use.

Opal glass for the intense tungsten light has been developed with a zinc oxide-alumina-borosilicate composition.

How we should live without glass is difficult to imagine. All factory work would depend on the weather, so costs would rise. Houses would be poorly lighted by day and without our lamp chimneys or our 400 million electric light bulbs per year (in America) there would be very little study or other reading by night.

Bottles for milk, medicine, and drinks would be lacking. We should know little of the stars and less of bacteria, and defective eyesight would go uncorrected. Photography and the motion picture would be unknown.

Enamels are glasses varied somewhat in composition. They are made white by suspended tin oxide or calcium phosphate or fluorspar.

Exercise 3.—How could you make a blue enamel?

Identified by color of flame - green.

Boron

Boron, with a valence of three, belongs with the aluminum family and not with tetravalent carbon and silicon. It is a more pronounced acid former than aluminum and in chemical properties is much nearer silicon.

Boron, prepared by reduction of its oxide with magnesium, has the interesting property of uniting, when hot, with both oxygen and nitrogen, but it has, as yet, no commercial use as the free element. Boron is hard enough to scratch rubies.

Occurrence.—The element is not found free but as boric acid, borax, boracite, rasorite, and colemanite. Boric acid, $B(OH)_3$, occurs in certain springs in Italy. On cooling, greasy, white crystals are deposited. Borax, $Na_2B_4O_7 \cdot 10\,H_2O$ is found in Death Valley, California. Boracite, a complex magnesium salt, is found in the Stassfurt mines. Colemanite, $Ca_2B_6O_{11} \cdot 5\,H_2O$, and rasorite, $Na_2B_4O_7 \cdot 4\,H_2O$, are plentiful in California.

Boric Acid, H_3BO_3.—Boric acid, as was mentioned, occurs in some hot springs. It is also prepared by acidifying borax solutions:

$$Na_2B_4O_7 + 5\,H_2O + H_2SO_4 \longrightarrow Na_2SO_4 + 4\,B(OH)_3.$$

Boric acid forms complex compounds with tungstic and molybdic acids, organic oxy-acids such as tartaric, and with itself as shown by such minerals as boracite, $B_{16}O_{30}Mg_7Cl_2$, a salt of $H_6B_8O_{15}$. It is very faintly acid and so its use as a mildly antiseptic eyewash is not complicated by hydrogen ions. There is some question about the existence of its salts. Purification of this acid is easy because it is volatile with steam. Identification is also easy since it imparts a green color to a gas flame. On heating to 100° it changes by partial dehydration to the metaboric acid, at 140° to tetraboric acid, and at high temperatures to the anhydride. Boron trioxide is a hygroscopic glassy solid melting at about 1300°.

(acidic) HBO_2 =

$$\underset{100^\circ}{H_3BO_3} \longrightarrow \underset{140^\circ}{HBO_2} \longrightarrow H_2B_4O_7 \longrightarrow B_2O_3$$

[illegible]

Since boron trioxide is not volatile below a white heat it expels more volatile anhydrides from their salts. For example:

$$K_2SO_4 + B_2O_3 \longrightarrow 2\,KBO_2 + SO_3.$$

Borax.—Borax crystallizes from solution at 56° with $5H_2O$ of crystallization and at 27° with $10\,H_2O$. It can be made by neutralizing boric acid, although this is not the method commonly used.

$$4\,H_3BO_3 + 2\,NaOH \longrightarrow 7\,H_2O + Na_2B_4O_7.$$

In 1926 the whole world's borax industry was disturbed by the opening of a huge deposit of kernite (rasorite) in the Mohave

Desert, California. This mineral is $Na_2B_4O_7 \cdot 4\,H_2O$, the same as borax, but with less water. Purification consists merely in dissolving the sodium borate, filtering off the clay impurity, and recrystallizing the product. This discovery must lower the cost of borax and ultimately make pyrex glass more common. (Why?)

Since borax is a salt of a strong base and a weak acid, its solutions are basic by hydrolysis. Of course, this hydrolysis increases with dilution, as may be shown by addition of silver nitrate to concentrated and dilute solutions. White silver borate is precipitated from the concentrated borax solution, but brown silver oxide from the dilute solution. In the latter case silver hydroxide is first formed, which with loss of water becomes the oxide. Since borax solutions are strongly basic it is useful in softening water and in cleansing. As a flux in soldering it has another use. The formula might well be written as $2\,NaBO_2 \cdot B_2O_3$, which shows that borax is really sodium metaborate with the acid anhydride. When melted between hot metal plates, as in welding or soldering, this acid anhydride reacts with metallic oxides (rust) to form easily fusible slags which are squeezed out, leaving clean metal surfaces for good contact. Borax is used in Jewelry glass, soaps, pottery, and enamels, in canning, as a preservative, and as an antiseptic. Half of it goes into pottery and enamels.

Borax beads are used in analysis in much the same way. Some powdered borax is picked up on a loop of platinum wire and heated in the flame to expel water of crystallization. A clear, glassy bead results. This is touched to a minute fragment of the substance to be tested and heated again. In the case of a cobalt compound, a blue bead results. Some cobalt oxide is formed on heating, and this reacts with the acid anhydride (B_2O_3) part of borax to form a cobalt borate. The blue glass really is a double salt, sodium cobalt metaborate, $2\,NaBO_2 \cdot Co(BO_2)_2$. Other compounds give different colored beads. These beads resemble the colored silicate glasses. In fact, polysilicates would serve as well as borax beads in analysis if they melted at convenient temperatures. Some enamels are of this type.

Borax solutions turn turmeric paper brown. Acidified borax colors a gas flame both yellow (due to the sodium) and green (due to the liberated boric acid).

EXERCISES

4. Hot boron unites with nitrogen to form a white solid. What must be the formula and name? What similar compounds have been studied?

5. In the electric furnace, boron unites with carbon to form boron carbide, one of the hardest substances known. What similar reaction and product have you studied?

6. Why is silicon so tremendously important in compounds? Has the free element any uses?

7. Why are we dropping the use of manganese dioxide in decolorizing glass?

8. Calculate the percentage composition of orthoclase ($KAlSi_3O_8$).

9. What weight of water of hydration can be obtained from 75 Kg. of borax? What is the percentage of water in the crystal?

10. Calculate the atomic weight of silicon from the following date: 95.52367 g. of silicon tetrabromide yielded 16.56868 g. silicon dioxide.

11. How much sodium silicate can be made from 400 Kg. of sand (90 per cent pure)?

12. How is "non-shattering glass" manufactured?

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CHAPTER XXXV

PHOTOCHEMISTRY

The term photochemistry is not to be restricted to photography alone, but refers to all chemical reactions influenced by light.

Science includes among light rays those that affect the eye and others such as the ultra-violet and X-rays which affect the photographic plate. The term light is further extended by physicists to include heat rays and wireless waves.

Wave-lengths are expressed in millimicrons, mμ, or in Ångstrom units (A).

$$1 \text{ m}\mu = 1 \text{ millionth of } 1 \text{ millimeter,}$$
$$1 \text{ m}\mu = 10 \text{ Angstrom units.}$$

The extreme wireless (radio) waves may be expressed in terms of kilometers. The wave-length of visible light ranges from 400 mμ for the shortest violet to 800 mμ for the longest red, a light octave somewhat analogous to the octave in music, based on a doubling of vibration frequency. The velocity of all light radiation is the same, hence an obvious relation between wave-length and the number of vibrations per second (vibration frequency). Lemon states that if we call the range of visible light one octave, the known radiation range is 60 octaves. The diagram below (not drawn to scale) represents this range.

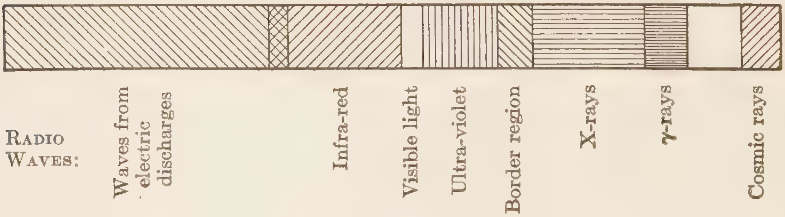


FIG. 125.—The octaves of light.

The Octaves of Light.—The electrical nature of light was first clearly postulated by Maxwell in 1873 and confirmed in 1888 by Hertz who created electric waves, of the type now used in radio, with properties similar to visible light waves. The former gap between radio waves and visible light has now been bridged, working from both ends. X-rays arise when electrons, radiating with lightning-like speed from the cathode in a high vacuum electric discharge tube (p. 265) strike a plate of metal (usually a tungsten "target"). Gamma rays, emitted from radium and similar elements, are similar but shorter in wave-length, while the cosmic rays (p. 450) from interstellar space are about three octaves higher yet.

The Unit of Light.—The heat effects of light are much greater in the infra-red than in the visible spectrum, while the chemical effects are greater in the upper range of the visible and just beyond in the ultra-violet. Planck assumes that "energy-elements of definite size are characteristic of light of a given frequency." This unit of light energy, the ***quantum,*** would be twice as large for violet light as for the red (corresponding to twice the vibration frequency).

The photoelectric effect of X-rays or ultra-violet rays on metals strengthens this conception. The velocity of the electrons torn loose from metallic surfaces by these radiations has no relation to the mere intensity or brightness of incident light (the greater the intensity the greater the number of electrons torn loose) but changes only with the color (vibration frequency) of the light. Presumably a single light-quantum is used up in liberating a single electron from the metal.

The electrons rotating around the nucleus of an atom are considered to exist at different energy levels. An atom is said to be in an "excited state" when one or more electrons are out of their normal energy levels. When such misplaced electrons return to their normal energy levels light is emitted, its frequency of vibration depending upon the energy difference. The transition is always abrupt.

Fluorescence, the emission by an illuminated substance of light of a different color from that of the exciting light, is illustrated by the visible glowing of teeth, bones, uranium glass, etc., in a *dark* room when invisible ultra-violet rays excite such substances.

Chemical Effects of Light.—It has long been recognized that it is only the absorbed light that influences chemical reaction. Photographs of the spectra secured when light passes through the substance to be studied may show an absence of certain usual lines. This indicates absorption of energy corresponding to the light vibrations responsible for such spectral lines. When such energy is absorbed some molecules of the illuminated substance must be made more active, or more reactive.

The effect of light in bringing about quick reaction between a mixture of hydrogen and chlorine was observed long ago. Toluene is chlorinated in the side chain, the CH_3 group, under the activating influence of ultra-violet light. It seems that chlorine is rather easily activated, for a number of reactions.

Rayleigh in 1911 found that nitrogen at low pressures is made chemically active by cathode rays. MacLennan froze nitrogen on the outside of a tube filled with liquid hydrogen and then bombarded the solid nitrogen with cathode radiations. The beautiful greenish-yellow luminescence persisted a short time after the discontinuance of the exciting radiations.

Two substances, otherwise unreactive under the influence of radiations that they do not absorb, may often be made to react by addition of a third substance that does absorb some of the light energy. Such substances, sensitizers, as they are called, are found among the dyes as in photograhpy. The element chlorine light-sensitizes the low temperature reaction between oxygen and carbon monoxide, but oxygen, on the other hand, strongly inhibits the photochemical chlorination of benzene. Light and a trace of moisture both speed up the union of bromine with ethylene ($C_2H_4 + Br_2 \longrightarrow C_2H_4Br_2$).

Silver bromide is far more readily reduced by green light than by yellow, for example, hence the use of orthochromatic films. These have been dipped in solutions of certain dyes capable of absorbing the longer wave-lengths of light.

Hemin, an iron compound in the hæmoglobin of red blood corpuscles, is marvellously sensitive to select radiations but not to all. One of its derivatives can sensitize a man so that he would be dangerously light-struck by ordinary daylight.

Light aids in the development of rancidity in fats, causes rubber to deteriorate, and converts cellulose of paper and cotton into oxycellulose with notable loss in strength.

Photography.—Photography, modernized picture-writing, is an essential tool for the astronomer, and is now coming to the aid of surveyors and military air-scouts in photographing mountainous or otherwise inaccessible regions. The physician, surgeon, and dentist rely upon X-ray photographs in the diagnosis of disease.

Even the historian uses photographs in reconstructing the past. Instruction and amusement lean heavily upon photography.

Scheele, famous for other brilliant works, discovered the photochemical decomposition of silver chloride in 1777, rightly blaming the darkening on sunlight and proving analytically that the silver chloride is decomposed to silver with loss of chlorine. Daguerre, about 1837, made the great discovery that an invisible image (latent) on silver iodide previously exposed in a camera, could be made visible, or developed, by fuming the plate with mercury vapor. Talbot, about 1839, advanced photography even more than did Daguerre (of "daguerrotype" fame).

The fundamental reaction in photography is that produced by the action of light on the silver halides:

$$2\ AgBr\ (\text{in light}) \rightleftarrows 2\ Ag + Br_2.$$

In the dark this reaction is slowly reversed. It is possible that one function of gelatin in sensitive films is to take care of the free chlorine or bromine. Probably a solid solution of silver in silver bromide is formed with release of some bromine. That chlorine is actually set free by the action of light on silver chloride has been proved by the smell. The loss in weight is as much as 8 per cent in a half-year, if the chlorine is allowed to escape. AgCl is not blackened by light if immersed in chlorine water above a certain concentration. The reaction must therefore be reversible. The sensitive film deposited on glass or celluloid is an emulsion (or, more accurately, a suspension) of silver halide in gelatin. (See chapter on Colloids.) By means of a lens an image is formed on the plate or film in the camera with varying intensities of light as reflected from white or darker objects. Thus the chemical effect of light on the silver halide varies throughout the film in accordance with the image. The image is said to be "latent" and is not visible to the eye until a developer (always a reducing solution) completes the reduction of the subhalide to metallic silver. From the developing bath the plate is taken to a "hypo" bath of sodium thiosulfate, which dissolves any unused silver halide. If this were not washed out, later exposure to the light would render the entire image uniform. The washed and dried negative is then a picture composed of varying thicknesses of metallic silver. This is printed on sensitized paper, which is merely a film much like that of the original plate, backed by paper. Silver chloride papers yield a visible image without further treatment. These are used for "proofs." To make them permanent they are washed with sodium thiosulfate solution to remove unused silver chloride and are then "toned" in a solution of a gold or a platinum salt. Metallic silver displaces gold from solution, thus converting the image on the paper into the rich red-brown of metallic gold. Platinum prints, prepared in a similar way, are steel gray.

If silver bromide papers are used, a latent image is obtained on printing. It is developed like the original plate. Since bromide papers are extremely sensitive, they are printed by artificial light.

The *development* of metallic silver seems to start from "centers" of sensitivity located on and in the silver halide crystals. Since different gelatins have been found to give very different sensitivities when used to make an emulsion by one and the same procedure it was suspected that a sensitizing impurity might be isolated. This was found to consist at least in part of certain organic sulfur compounds.

As S. E. Sheppard writes, "A typical developing solution will consist of the following:

a reducing agent, such as pyrogallol,
an alkaline accelerator, such as sodium carbonate,
a preservative, such as sodium sulfite,
a restrainer, as potassium bromide,

the whole dissolved in water. The sulfite should be dissolved first, and then the reducing agent, since the sulfite is acting as an antoxidizing agent to protect the reducer from aerial oxidation."

$$2\,AgBr + 3\,\underset{\text{"hypo"}}{Na_2S_2O_3} \rightarrow 2\,NaBr + \underset{\text{soluble}}{Na_4Ag_2(S_2O_3)_3}.$$

The silver halide particles in a film are crystalline; even those beyond the resolving power of the microscope show crystalline structure by the X-ray test.

In most negative emulsions enough potassium iodide to weigh about five per cent of the silver halide is added so that the resultant silver bromide contains a small amount of silver iodide. The printing papers may contain silver bromide and chloride, or even silver chloride.

The Photochemistry of Plants.—One of the most important problems facing scientists is the discovery of the secret processes by which nature in the green leaf converts radiant energy of the sun into sugars, starches and cellulose. Yet marvellous as is this photochemical conversion of carbon dioxide and water into more complicated compounds, it must be admitted that nature is wasteful.

"Energy from the sun pours on every acre of ground an equivalent of 1,476 tons of coal during an average 90-day growing season in our Middle West. Of this wealth of power a crop of wheat yielding fifty bushels to the acre, a very high yield, puts into the bin an energy equivalent of less than two-thirds of one ton of coal." (H. A. Spoehr.)

All the vast amount of carbon dioxide thrown into the atmos-

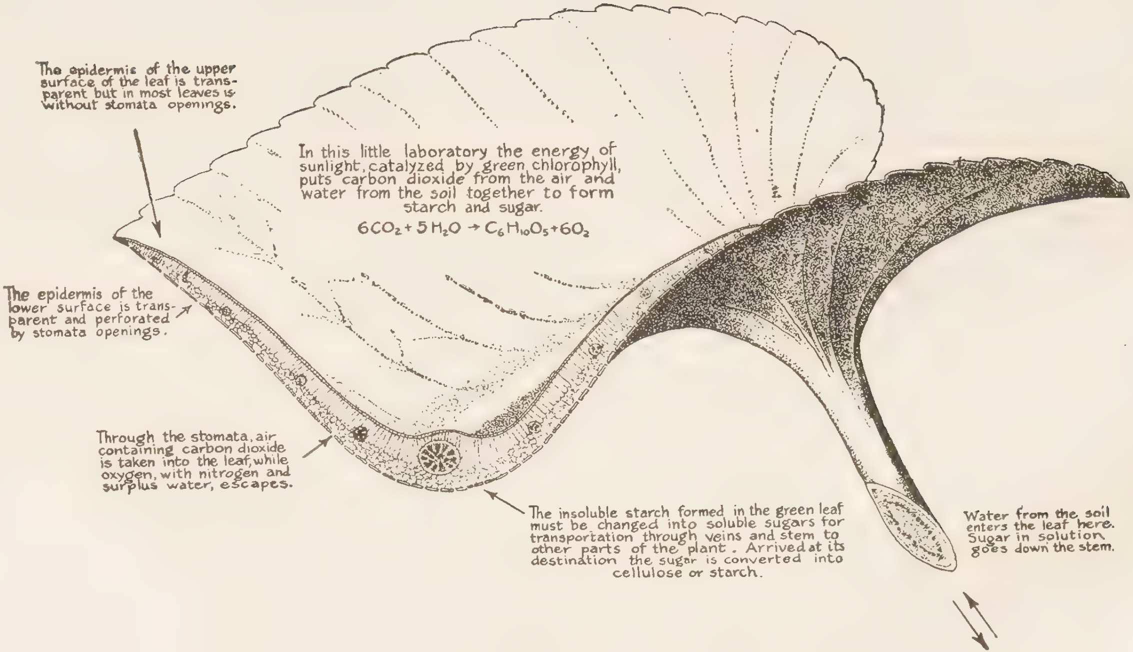

The epidermis of the upper surface of the leaf is transparent but in most leaves is without stomata openings.
In this little laboratory the energy of sunlight, catalyzed by green chlorophyll, puts carbon dioxide from the air and water from the soil together to form starch and sugar.
$6CO_2 + 5H_2O \rightarrow C_6H_{10}O_5 + 6O_2$
The epidermis of the lower surface is transparent and perforated by stomata openings.
Through the stomata, air containing carbon dioxide is taken into the leaf, while oxygen, with nitrogen and surplus water, escapes.
The insoluble starch formed in the green leaf must be changed into soluble sugars for transportation through veins and stem to other parts of the plant. Arrived at its destination the sugar is converted into cellulose or starch.
Water from the soil enters the leaf here. Sugar in solution goes down the stem.

FIG. 126.—The green leaf laboratory.

phere by processes of combustion, of decay, fermentation, and animal respiration is eventually taken up by plants as invaluable food. In the sunlight chlorophyll, the green coloring matter of leaves, is formed and catalyzes the following reaction (probably in stages):

$$6\ CO_2 + 5\ H_2O \longrightarrow C_6H_{10}O_5 + 6\ O_2.$$

But for this return of oxygen to the air, we should eventually suffer from an oxygen famine and animal life would cease. This $C_6H_{10}O_5$ is starch which may be rearranged into cellulose, the woody fiber of plants. The wonderful laboratory in the green leaf can change starch (insoluble) into soluble sugar for transportation to parts of the plant needing new material. It is there changed again into starch or cellulose.

When wood is burned or starch or sugar eaten, all the carbon dioxide given off goes through the same cycle. The perfection of the whole process is shown by the return of oxygen to the air, ready to support life or combustion. Furthermore all the energy absorbed in the reaction between carbon dioxide and water is obtained or made available when the sugar, starch, or cellulose is eaten or burned.

The first recognizable product of the process, according to Baly, can be written

$$6\ H_2CO_3 \longrightarrow C_6H_{12}O_6 + 6\ O_2,$$

where the $C_6H_{12}O_6$ is either glucose or fructose. The simple sugars at once condense to cane sugar or starch. The sensitizer is green chlorophyll. Others have shown the presence of traces of formaldehyde when carbon dioxide and water were irradiated with ultra-violet light and Baly himself stated that formaldehyde was converted by light into glucose and fructose. Baly holds that the formaldehyde is a decomposition product of carbohydrates under certain conditions. Baly reports that the efficiency of this photochemical process (occurring even in red light) is greatly increased by the presence of finely divided solids such as aluminum hydroxide, especially if some colored substance had been added. He is sure that both surface energy and radiant energy are essential to the synthesis.

Ultra-violet Light.—Light waves from the sun extend into the ultra-violet region to about 290 mμ, all shorter being absorbed in passing through our atmosphere. The rays from this limit of 290 mμ to about 310 mμ have been shown to be very beneficial in the cure of rickets, surgical tuberculosis, in hastening the cure of wounds, and in improving the general health and growth of those receiving such radiations.

Ordinary glass transmits a portion of the ultra-violet nearest the visible region of the spectrum, but entirely eliminates vital rays between 290 mμ at 310 mμ. Quartz glass is very transparent to such waves but is extremely expensive.

A few commercial glasses with very good ultra-violet transmission have been developed recently for sun rooms and hospitals, and cheaper substitutes for chicken houses. One of the best is a phosphate-silicate glass. It must be remembered, however, that patients are benefited only when exposed to the direct ultra-violet rays passing through such windows. "Pollopas," a new product formed from formaldehyde and urea, is exciting interest because it is very permeable to ultra-violet light as well as the visible, and is reasonably hard and strong. Such a material is needed. The remarkable opacity of potassium hydrogen phthalate solutions to ultra-violet light is shown by the fact that a one-millimeter layer of a 4 per cent solution cuts off ultra-violet sharply at 300 mμ although transmitting the visible light.

The iron arc is a rich source of ultra-violet but the most powerful is the mercury vapor lamp (in a quartz tube). Both are used in preventing or curing rickets in children and in a general toning up of animal health.

The sun's ultra-violet light, especially shorter wave-lengths that are cut off by the miles of air in our atmosphere, converts the dry upper oxygen into ozone, and perhaps ionizes some of the air, forming a downward-reflecting ceiling for radio waves.

There are various reactions by which ultra-violet may be detected but its decomposition of pure carbon tetrachloride will suffice as an illustration:

$$2\,CCl_4 \longrightarrow C_2Cl_6 + Cl_2.$$

The exposed liquid is shaken with a very little water solution of potassium iodide. The chlorine set free displaces iodine, which gives a color to the carbon tetrachloride to be compared with known-strength color standards. The freed iodine may also be titrated against standard strength solutions of sodium thiosulfate.

X-rays produce profound physiological changes in the animal body and so are used in treatment of certain types of skin diseases, even in surface cancers.

The Photoelectric Cell.—Electric currents have been generated when one of two connected metallic plates was illuminated. Recently a cell, remarkably sensitive to light, has been constructed by using for one plate a layer of rubidium, one atom in thickness, deposited on glass.

"Metals differ in power of emitting electrons under illumination. Best conditions are obtained by putting the metal in a glass or quartz enclosure, and controlling both the kind of atmosphere and its pressure. The more electro-positive the metal, the more photo-sensitive; so in place of zinc and copper, in the earlier studies, an alkali metal, potassium, rubidium or cæsium, is used in non-reacting atmospheres—an inert gas, argon, helium, or neon—at a low pressure suitable for multiplying the photo-current by the electric conduction induced in the gas by collision of the electrons with the gas atoms.

"The typical photoelectric cell is a glass bulb, with one electrode, the cathode, usually a layer of alkali metal on the inner surface, with a wire leading out through the glass, and another electrode, the anode, a loop of wire, likewise carried out. Connect these two wires through a galvanometer and let light shine into the bulb; the galvanometer will show an electric current flowing. The current starts and stops instantaneously; it is proportional to the illumination. It is quite small, but with proper instruments it may be used to measure the intensity of light from such faint objects as sixth magnitude stars." (Herbert E. Ives.)

With an outside electromotive force, as from a battery, these electrons or ***photoelectrons*** as they are termed when driven out of atoms by radiations, will carry the current through the photoelectric cell.

Cosmic Rays.—Milliken in 1926 identified mysterious radiations of the highest frequency, the "cosmic rays," coming to us from interstellar space. They penetrate 200 feet of water or 18 feet of lead. Milliken believes that:

"1. Positive and negative electrons exist in great abundance in interstellar space.

"2. These electrons condense into atoms under the influence of the conditions existing in outer space, absence of temperature and high dispersion.

"3. These atoms then aggregate under their gravitational forces into stars.

"4. In the interior of stars, under the influence of enormous pressures, densities, and temperatures existing there, an occasional positive electron, presumably in the nucleus of a heavy atom falls into complete coincidence with a negative electron, fritters its entire mass into an ether pulse the energy of which, when frittered away in heat, maintains the temperature of the star and furnishes most of the supply of light and heat which it pours out.

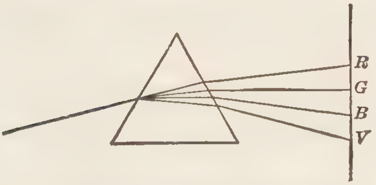


FIG. 127.—Dispersion of light by a prism.

"The observed cosmic rays are in fact the birth cries of the infant atoms of helium, oxygen, and silicon, with perhaps shriller squeaks from the infant iron."

The Spectroscope.—A beam of sunlight passing through a transparent prism is dispersed into the colors composing white light (Fig. 127). This is due to the fact that in entering one transparent medium from another the different wave-lengths of light are bent in different degrees. Against a white screen these colors are projected in a band called the spectrum. The spectro-

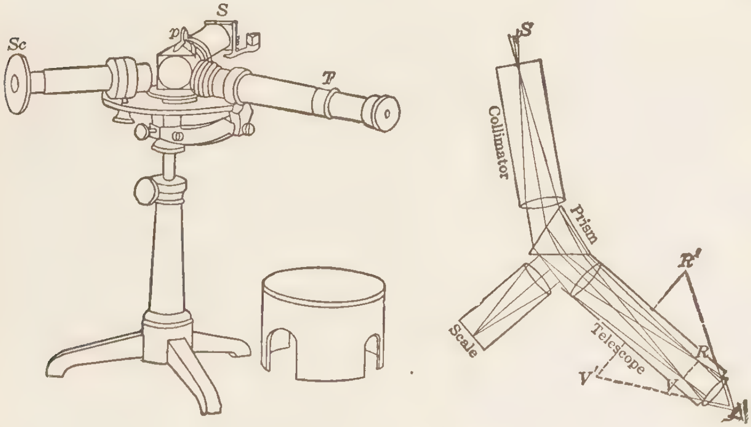


FIG. 128.—The spectroscope.

scope (Fig. 128) consists of a glass prism, a tube containing lenses and an adjustable slit to admit a narrow beam of light, a telescope with which to view the spectrum, and a third tube which projects the image of a measuring scale on the field. Small direct-vision spectroscopes are made of a single tube with lens, prism, and slit inside the tube.

Wave-lengths shorter than the visible are called "ultra-violet" and have considerable actinic power. They are the cause of sunstroke and probably convert some of the oxygen of the upper atmosphere into ozone. Heat waves are longer than the visible wave-lengths.

Bright-line Spectra.—An incandescent solid gives a continuous spectrum of all wave-lengths. An incandescent gas gives a spectrum made up of one or more bright lines, sometimes a large number. These are always characteristic of each element, both in color and in the exact position of the lines. For example, if light from a sodium flame is viewed through the spectroscope, a single yellow line is observed. Incandescent helium gives a spectrum of definitely located red, yellow, green, and blue lines, and may be recognized by them.

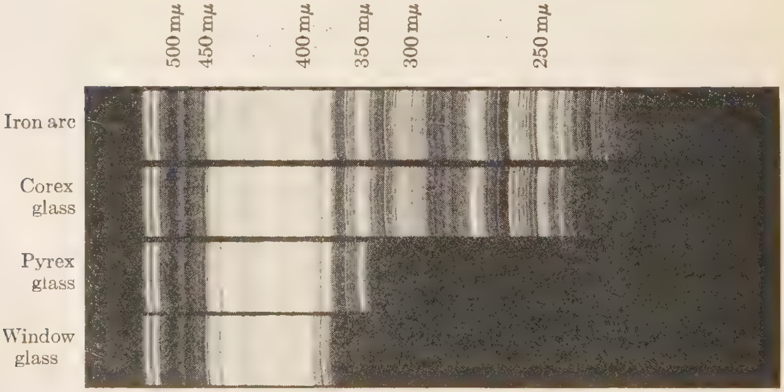
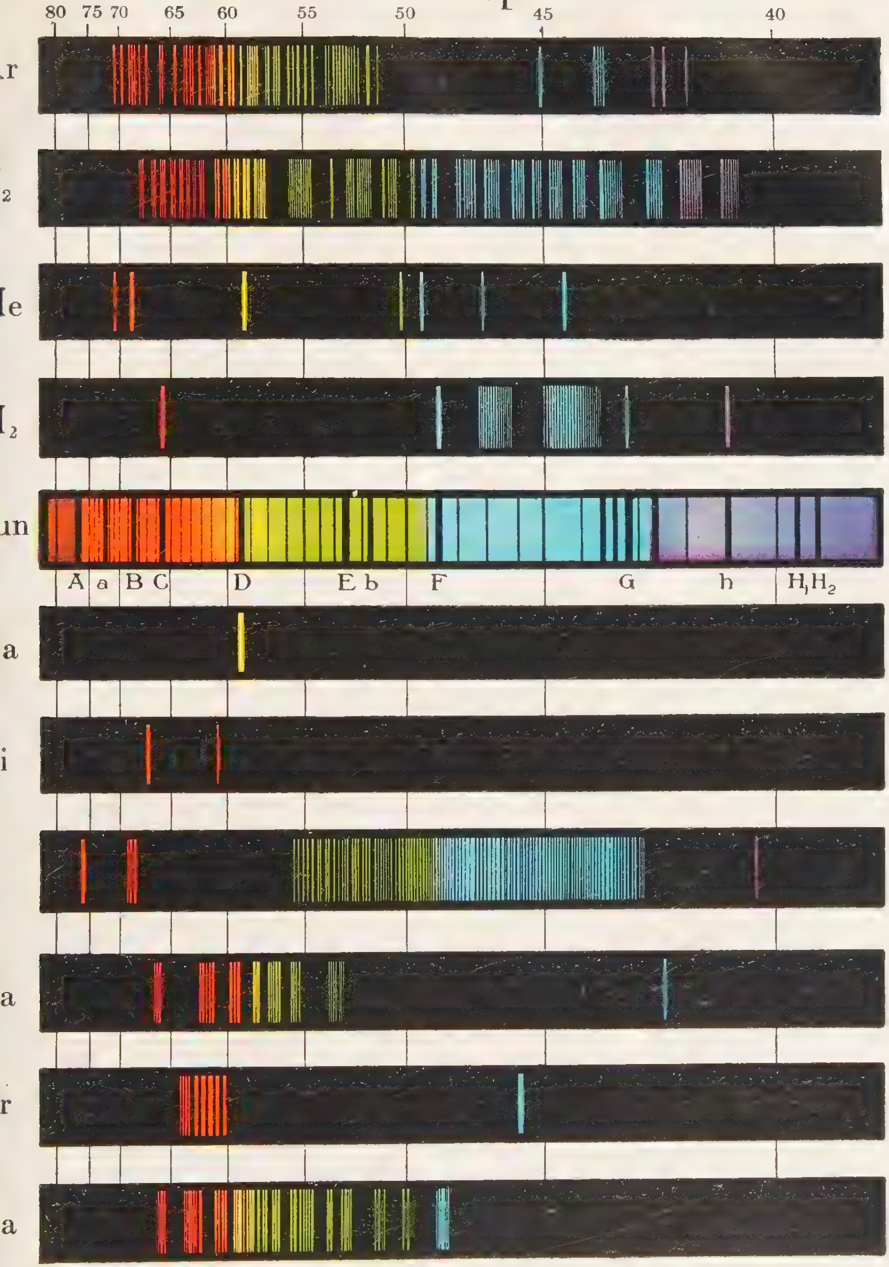


Fig. 129.—Spectrogram showing the transmission of ultra-violet light (from the iron-arc lamp) by three glasses.

Dark-line Spectra.—The spectrum of the incandescent sun is really not continuous but contains many dark lines (Frauenhofer lines, because they were first mapped by Frauenhofer in 1814). These are explained by the fact that when, for example, light from

Plate of Spectra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From *Inorganic Chemistry*, by H.P. Cady.
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a white-hot solid passes through a yellow sodium flame there is a dark line in the yellow part of the spectrum. In other words, a gas which, when incandescent, is capable of producing certain definite lines in the spectrum absorbs those very lines from light passed through the gas. It is evident, then, that the gaseous envelope around the sun absorbs certain wave-lengths of light and gives us a dark-line solar spectrum instead of a continuous one. Due to this fact we learned of the existence of helium in the sun's atmosphere thirty years before it was found on earth. Included in the solar gases are the terrestrial elements, sodium, calcium, iron, hydrogen, manganese, carbon, silver, and others to the number of forty or more.

Liquids absorb certain wave-lengths, giving a dark-band spectrum. Without question the spectroscope is a delicate and invaluable analytical tool.

EXERCISES

1. Define photochemistry, wave-length, Ångstrom unit, quantum, fluorescence, ultra-violet light, bright-line spectra, dark-line spectra.
2. List some familiar chemical reactions which are brought about by light.
3. What becomes of the light energy absorbed in a solution?

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CHAPTER XXXVI

COLLOID CHEMISTRY

Colloid chemistry is closely related to the problems of lubrication, agriculture, de-watering oils, purifying clays, catching offensive or wasted fumes, drying peat, de-inking old newspapers, concentrating ores, tanning, baking, cooking, washing, dyeing, roadmaking, photography, water purification, sewage disposal; and one should know a good deal about colloid chemistry if he is to manufacture rubber goods, glass, porcelain, enamels, cements, alloys, fungicides and insecticides, dairy products, any cellulose ester materials, colloidal fuel, gelatine, glues, gas masks, adsorbent gels, paints, varnishes, soap, inks, oils, pencils, and crayons.

Strictly speaking, there are no such things as ***colloids,*** for most if not all, substances can be prepared in the "colloidal state." However, the term ***colloid*** is too convenient to drop.

"Colloid chemistry," writes Bancroft, "is the chemistry of grains, drops, bubbles, filaments, and films." This is a useful conception. By grains we mean small solid particles. Drops are small liquid particles, and bubbles small gas particles. In filaments, all dimensions but one are very small, while in films only one dimension is small. These particles must be surrounded by, or dispersed in, some other substance.

But after all we are colloidally interested in grains, drops, and bubbles only when they are sufficiently small, of diameters ranging from about 100 mμ to 1 mμ. (A millimicron, 1 mμ, is one millionth of a millimeter.) The smallest particle visible with the aid of the best microscope is about 100 mμ in diameter, while the largest molecules approach a diameter of 1 mμ. The colloidal realm ranges, then, from the lower limit of microscopic visibility to the upper limit of molecular dimensions. Most colloidal particles are aggregates of hundreds or thousands of moleclues. Yet the largest molecules exhibit some of the surface phenomena of colloids. When colloidal units or aggregates coalesce into still larger aggregates they may be precipitated from suspension. Unless such coagulated material becomes distinctly crystalline on standing, we are in the habit of calling it colloidal, as in the case of cheese, for example.

New properties of matter appear when a given substance is colloidally dispersed. The effect of gravity is counteracted somewhat, while surface tension, electric charge, and other forms of energy increase greatly. Gold, yellow in the mass, may be dispersed in water to form what is apparently a blue solution. With still finer dispersion it is red, and then just short of molecular dispersion. The brightest red particles of gold are about 6 mμ in diameter.

Grains	dispersed in another solid	gold in ruby glass sodium in blue rock salt elements or compounds in some alloys
	dispersed in a liquid	colloidal gold in water colloidal selenium in water
	dispersed in a gas	dust visible smoke
Drops	dispersed in a solid	water in butter
	dispersed in a liquid	oil-in-water emulsions (milk)
	dispersed in a gas	mist fog
Bubbles	dispersed in a solid	air in meerschaum air in pumice stone
	dispersed in a liquid	foam
	dispersed in a gas	impossible because gases form molecular mixtures
Filaments	any solid fibrous material may contain filaments of minute diameter	
Films	films may be liquid or solid, but they must be very thin; soap bubble films have one colloidal dimension	

It may be roughly stated that acids, bases, salts, sugars, and crystalline substances in general are molecularly dispersed in water solution, while the glues, gums, resins, starch, cellulose, rubber, and non-crystalline substances in general are colloidal, that is, dispersed in particles much larger than molecules.

Yet this statement must be qualified, for sodium chloride is in true solution in water and in colloidal dispersion in certain organic liquids. Many substances previously called amorphous (noncrystalline) and colloidal have recently shown an ultramicrocrystalline structure under the searching eye of the X-ray. However this makes no difference in our definition for the colloid conception is now solely that of size of particle.

Add a saturated solution of mercuric chloride to a brown suspension of colloidal silver. The color disappears, and a white precipitate of mercurous chloride and silver choride is found. ($HgCl_2 + Ag \rightarrow AgCl + HgCl$.) In this case the reducing action of silver has been greatly magnified, due to its relatively great surface.

Why Colloidal Particles Remain in Suspension.—Gold is much heavier than water, yet red-gold suspensions in water have been kept for many years without settling. If the water were frozen to solid ice, we might understand this non-settling, as we do in the case of ruby glass. There are at least three good reasons for the stability of ordinary colloid suspensions. These are the Brownian movement, the presence of electric charges on particles and of protecting films around them.

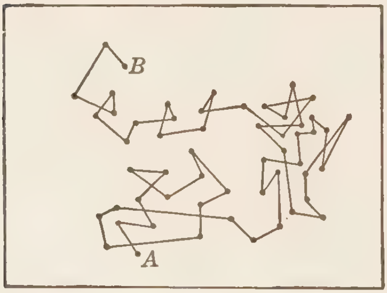

FIG. 130.—Brownian movement.

1. ***Brownian Movement.*** If a heavy steel ball were suspended by fine wire, a light tap with a pencil would certainly move the ball, almost imperceptibly. The same light tap of the pencil must move a suspended baseball quite appreciably, and must produce exaggerated motion in a light pith ball. In each case the kinetic energy is the same, so the greater the mass of the ball, the less the distance moved.

In order to magnify the distance moved by a bombarded particle it is only necessary to diminish the size of the particle sufficiently. Consider a colloidal gold suspension. The water molecules, always in constant motion when above absolute zero, bombard the suspended particles of gold from all sides. The gold particles are moved some distance, of course, but when such particles are large enough to be visible, this motion is too slight to be of much help and the gold settles rapidly. But gold aggregates under 100 $m\mu$ in diameter are projected appreciable distances by the water molecules. This vigorous stirring effect is perpetual. Under the lens of the ultra-microscope this Brownian movement is startling. The gold particles dart with zigzag motion an all directions (Fig. 130). At this point the observing student remembers that colloidal gold particles are not visible under the microscope. How then is this motion apparent? The suspension is examined in a dark field while a strong beam of light entering at right angles to the line of vision makes the gold particles visible as mere points of light without apparent diameter. This Brownian movement furnishes convincing proof of the reality of molecules, the molecules that do the bombarding.

The suspended colloid particles must have kinetic energy of their own just as truly as have the molecules, but, being heavier, their actual motion is less. The impacts against one side of a very small colloidal particle are not always balanced by impacts of equal force on other sides. The result is that colloid particles actually travel in a zigzag path.

2. *Electric Charge.* Most colloid particles move slowly in an electrolytic cell as if attracted by the charged poles and are coagulated into coarse aggregates on contact with the attracting poles. This means that the particles are electrically charged bodies. In some suspensions, such as arsenic sulfide, all the particles are attracted to the anode, hence are negatively charged. Ferric hydroxide particles are all positive. Particles bearing like charges, free to move, must repel each other, thus tending to remain scattered or suspended throughout the liquid.

3. *Protecting Films.* A film of gelatin or of various gummy substances can surround each suspended particle so that they have difficulty in touching. Under such conditions coalescence into aggregates too large for help from the Brownian movement is difficult. Any influence tending to keep the aggregates small aids stability.

Methods of Preparation.—There are several methods of subdividing the common insoluble substances so that the substances become colloidally suspended. Some methods are purely mechanical and others are chemical. It must be remembered that although these suspensions may look like true solutions to the eye, they are not true solutions. The effect of suspended material on osmotic pressure, freezing-point lowering, and boiling-point rise is trifling, as might be expected from the smaller number of particles per gram of suspended matter as compared with number of particles (molecules) from a gram of matter in true solution. Most colloid aggregates are hundreds or thousands of times as large as a molecule. We have not yet found a molecule of colloidal size.

Reaction between dissolved substances may yield precipitates or may yield colloidal aggregates. In the latter case colloidal suspensions are formed by ***condensation*** of smaller particles into larger ones.

Dispersion methods are the exact opposite of condensation methods: larger particles are broken down into smaller.

Dispersion Methods.—1. ***Mechanical Disintegrations.*** The simplest method in principle but not always suitable in practice, is fine grinding. Most of the modern "colloid mills" have two rotating parts (high speed) with very small clearance. Material that is not too hard is disintegrated but not really into particles of 1 to 100 mμ dimensions.

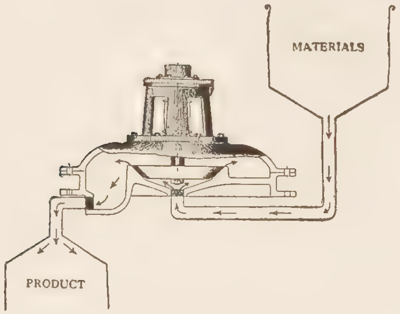

FIG. 131.—A colloid mill.

2. ***Peptization by Liquids.*** By peptization we mean disintegration into colloidal particles through the action of some added chemical. Water has long been used as a peptizing agent in *dissolving* glue, gelatin, agar, and such substances. In reality, the glue or gelatin was not dissolved in the true sense of molecular dispersion, but only colloidally dispersed. Hot water has a more rapid peptizing action than cold. Acetone is said to dissolve pyroxylin but it only peptizes the solid.

3. ***Peptization with Ions.*** Colloid particles have an ability to hold to their surfaces, to adsorb other substances, even ions. A given surface may have a preference for certain ions and thus in one case acquire a positive charge by holding a positive ion, charge and all, while another kind of colloid may choose to acquire a negative ion and charge. This reminds us of one of the reasons for stability—like charges on the particles with consequent repelling or stirring action. It is thus evident that a colloid may be stabilized, kept in suspension, by adsorption of ions.

Precipitates are sometimes peptized by washing out the precipitating ions. This really means that the proper ionic concentration for suspension is secured. In analysis precipitates are often inclined to run through the filter on washing. Wash waters containing ammonium salts are then used to coagulate the suspension. Fortunately such salts may later be removed by ignition.

Silver bromide formed in the presence of a slight excess of Ag^+ ions fails to precipitate. The absorbed Ag^+ ions give their positive charge to the silver bromide particles, thus suspending them. With a slight excess of Br^- ions the suspension is negatively charged, due to preferential adsorption of negative Br^- ions.

4. *Bredig's Electric Arc Method.* If two gold wires properly insulated with glass tubes are connected with a 110-volt circuit through sufficient resistance to yield a current of about 10 amperes, and brought close together under water, a small arc forms with violent disruption of the gold. Coarse particles and fine, suspended together, make the water cloudy. A mere trace of sodium hydroxide in the water is a great help, possibly because adsorption of a few hydroxide ions stabilizes the gold. After filtration, a red suspension is obtained. In practice, the simplest manipulation is to bring the wires together rapidly and repeatedly for several minutes.

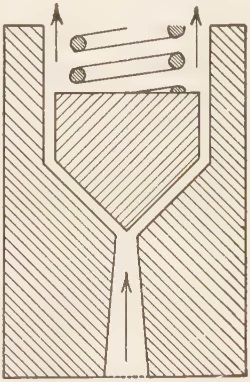

FIG. 132.—A homogenizer for reducing the size of droplets in emulsions. The spring is set so that the needle valve is forced open when liquid enters at a pressure of 2000 pounds.

5. *Emulsification.* One liquid may be dispersed in a second (if they are immiscible) by mere shaking or stirring, but such dispersions, or ***emulsions,*** are temporary, quickly separating into their components. To make emulsions is easy; to keep them is the problem.

Shake water and kerosene together. On standing, the high surface tension of the water drops pulls them into one big drop or layer because of the tendency to expose the least possible surface. By lowering this surface tension of water the emulsion should keep longer. Shake kerosene with a 1 per cent aqueous solution of sodium oleate (a soap which greatly lowers the surface tension of water). A thick, creamy emulsion of drops of oil dispersed in water results and keeps fairly well. As in the case of milk, an emulsion of fat globules in water, etc., a cream slowly separates. This is merely a layer of a richer emulsion above a poorer one.

Now add any acid to this emulsion. It breaks because the added acid destroys the soap, the emulsifying agent. Other emulsifying agents than soaps are possible. Gelatin can be used for kerosene-in-water. Gum arabic is useful, and with the proper liquids cellulose nitrate will serve. Mayonnaise is an emulsion of olive oil in water (or vinegar), with the colloidal albumen of the egg as emulsifying agent.

It is impossible to make a lasting emulsion of more than 1 per cent dispersed phase with two pure liquids—a third substance is necessary as an emulsifying agent and this must be colloidal.

By slowly adding an oil to soapy water with vigorous agitation, Pickering made an emulsion of 99 per cent oil (as separate drops) and 1 per cent water (films between the drops). This emsulion when cut into a cube retained its shape on a flat plate.

Surface tension lowering often exerts considerable influence in emulsification. Concentration of the emulsifying agent into adsorption films around the drops is usually the leading factor in preventing coalescence.

With the aid of the proper emulsifying agents it is possible to make emulsions of the two types shown in Fig. 133.

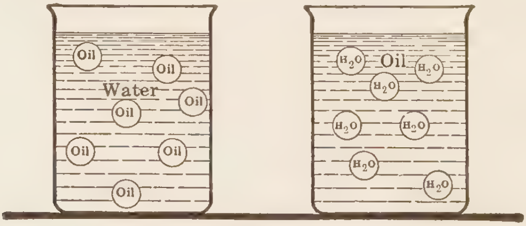

Fig. 133.—Two types of emulsions.

Using sodium, potassium, or ammonium soaps as agent, the oil is dispersed in water (the usual type), but with calcium or other alkaline earth soaps water is dispersed in drops throughout the oil (the unusual type, a water-in-oil emulsion). This is because alkaline earth soaps are more soluble in oil than in water. A rule applicable here is that if the emulsifying agent is more readily peptized by liquid A than by liquid B it will be B that is dispersed in drops. This is even true in the case of insoluble fine powders which are more readily wetted by A than by B. There are few exceptions to this general rule.

Condensation Methods. 6. ***Reduction.*** Salts of gold, silver, mercury, platinum, and palladium in water are easily reduced to the free metal. Under favorable conditions beautiful suspensions form. Very dilute gold chloride solutions made neutral by a trace of potassium carbonate are reduced almost too easily. Casual impurities, such as those introduced by contact with the finger, may produce red or blue gold.

Mix 2 cc. of 1 per cent gold chloride solution with 98 cc. of water. Dissolve 0.5 g. tannin in 100 cc. water. Heat both solutions and mix equal parts, adding one to the other rather slowly. A clear red or blue suspension results.

To 5 cc. of 1 per cent silver nitrate add very dilute ammonium hydroxide, drop by drop, until a precipitate just disappears. Dilute with 100 cc. of water. Add an equal volume, or less, of tannin solution (0.5 g. in 100 cc. water). Here the tannin reduces the silver oxide to colloidal silver. As with gold the color varies with the size of particle. Colloidal silver may be cherry-red, brown, or greenish-brown.

Fehling's solution contains a copper complex (tartrate) which is reduced by glucose to yellow-red cuprous oxide. Sometimes rather unstable suspensions of cuprous oxide are made showing one color by transmitted light and another by reflected light. This is the test applied to urine in diagnosing diabetes.

7. ***Formation in Low Ion Concentration.*** A familiar reaction is that between hydrogen sulfide and arsenic trichloride:

$$(1)\ 2\,AsCl_3 + 3\,H_2S \longrightarrow 6\,HCl + As_2S_3.$$

The yellow sulfide settles out quickly. Yet if some arsenious oxide is boiled in water and the solution filtered, any addition of hydrogen sulfide fails to yield a precipitate. A lemon-yellow suspension is obtained:

$$(2)\ As_2O_3 + 3\,H_2S \longrightarrow 3\,H_2O + As_2S_3.$$

The essential difference between (1) and (2) is that in (1) the by-product is an acid which ionizes, while in (2) the by-product is only water. Addition of a little hydrochloric acid or even some salt to the yellow colloid suspension coagulates the sulfide, with consequent quick settling. The suspended particles are negatively charged, and it is obvious that this charge could be neutralized by positive ions, such as hydrogen, sodium, and others. Loss of charge means less ability to remain suspended.

To secure a suspension of any insoluble salt while forming, there is required an absence of oppositely charged ions or at least a very low concentration of such ions.

8. ***Hydrolysis.*** If to any dilute solution of ferric chloride hydrochloric acid is added, the distinct reddish-brown tint changes to a pure yellow, that of ferric chloride. Ferric chloride is readily hydrolyzed with formation of ferric hydroxide:

$$FeCl_3 + 3\ H_2O \rightleftarrows 3\ HCl + Fe(OH)_3.$$

It is this colloidal ferric hydroxide that gives solutions their reddish-brown color. Addition of hydrochloric acid drives the reaction to the left (by mass action) and the hydroxide is largely converted into the chloride. Higher temperatures favor hydrolysis. If into a beaker of boiling water a few cc. of 30 per cent ferric chloride are poured, a rich red colloidal suspension of ferric hydroxide forms instantly. This is a useful preparation because it is a typical positive colloid and keeps a long time. Hydroxides of aluminum and chromium may be made, but not quite so easily. Other methods are preferred for them.

Dialysis.—Making colloids is one matter, keeping them is another. Since ions of opposite charge tend to coagulate suspensions, a measure of safety should be secured by removing these ions. Fortunately there is a method for accomplishing this, namely, dialysis.

Many membranes, such as bladder, intestine, peritoneum, parchment paper, egg skin, and the like, are permeable to water and ions but not to the larger aggregates known as colloids.

To show dialysis quickly, tie a sheet of goldbeater's skin or wet parchment paper free from pin holes over the mouth of a bottle from which the bottom has been removed by cracking. A wide-mouthed bottle is preferred. Invert the bottle in a large beaker of water and fill with cold, freshly made colloidal ferric hydroxide. This is a mixture of water, colloidal aggregates of ferric hydroxide, and the ions of hydrochloric acid. The smaller ions and molecules pass out through the membrane, and if the outer water is frequently changed they are almost completely removed, leaving only ferric hydroxide suspended in water. The last trace of ions is often difficult to remove and may even be necessary to the stability of the colloid. A bag of parchment paper, bladder, goldbeater's skin, or collodion may be filled with the suspension to be dialyzed and suspended in a beaker of water as in Fig. 134.

In trying the experiment with colloidal ferric hydroxide samples of the dialysate (corresponding to filtrate) should be removed in a few minutes, and tested with silver nitrate. The passage of chlorides through the membrane is very rapid.

Cellophane Sausage Skin Dialyzers.—The recent development of artificial sausage skins from tubular forms of viscose (cellophane) has given the colloid chemist a valuable tool. These membranes are very permeable or rapid in action and most convenient in form. The usual form is about 1 inch (2.5 cm.) in diameter but a large size with thicker wall (about 8 cm.) may be obtained. The cost is low. Purchase from the Visking Corporation, 4311 Justine Street, Union Stock Yards, Chicago.

Close one end of a sausage skin by tying a tight knot with strong cord, insert a funnel in the other end of a convenient length and pour in any convenient colloid sol. Tie the upper end around a glass rod, or insert a cork stopper in it and support in any way desired. Hang it in a vessel of pure water, coiling it around the wall if desired and observe the passage of ions through the viscose membrane. These membranes need not be kept wet like collodion membranes.

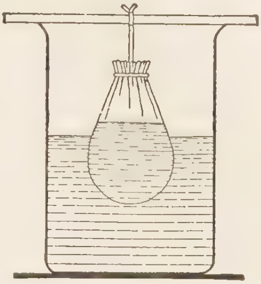

Fig. 134.

Greater lengths must be supported by coiling in the vessel of water as filling proceeds.

To make collodion dialyzers fill a dry tube or an Erlenmeyer flask, invert, and clamp to drain for a few minutes. When no ether is noticeable, fill with warm water and carefully loosen the membrane. By using beakers, larger cups may be made. Permeability depends on the extent of drying before water is added to loosen the film. Large sheets may be formed on a tray of mercury but a cover should be used to check too rapid loss of ether.

Classification.—Examples of the ***suspensoid state*** are found in colloidal gold, silver, arsenic sulfide, and ferric hydroxide. These are easily coagulated by very small quantities of electrolytes and have a viscosity but little more than that of the liquid in which they are dispersed. Water containing 20 per cent of barium sulfate in suspension is stirred about as easily as water alone. Suspensoids do not gelatinize.

Examples of the ***emulsoid state*** are found in water suspensions of gelatin, agar, glue, starch paste, soaps, egg albumin, silicic acid, and the like. These are coagulated only by relatively large quantities of salts and are extremely viscous. A 1 per cent suspension of agar in water is a solid jelly at room temperatures as is a 1 per cent suspension of sodium stearate soap.

If evaporated to dryness, or coagulated, the suspensoids are ***irreversible,*** that is, they cannot be suspended again. The emulsoids after evaporation are easily thrown into suspension again and so are ***reversible.*** Of course there are gradations between these two states.

Adsorption.—A cube 1 cm. on edge has a surface of 6 sq. cm. If subdivided into smaller cubes, each only 100 mμ on edge, the total surface is 600,000 sq. cm. and there are 10^{15} particles. If further subdivided into the colloidal realm of 10 mμ on edge, the total surface becomes 6,000,000 sq. cm. In number the particles have grown from one to 10^{18}. This vast increase of surface magnifies all surface influences. Adsorption has already been mentioned as a holding of various substances to specific surfaces. The adsorptive power of a definite weight of carbon, for example, may be vastly increased by subdividing the carbon. Bone charcoal is used in sugar refineries to decolorize sugar syrup by adsorption of coloring matter. A sugar refiner buys this carbon for its surface, so size of particle means something to him.

Adsorption of toxic gases by cocoanut charcoal is familiar to all after the experiences of the World War. Yet the application of the principles of gas adsorption by activated carbon, silica gel, etc., is now a peace-time matter of great commercial importance. Silicic acid, formed as a gel, washed, and dried to a content of 5 per cent water, is a glassy material shot through with innumerable capillary pores of diameter not much greater than that of molecules. In these capillary pores gases are brought well within the range of molecular attractive forces, and so are held or "adsorbed." This adsorption is preferential for various gases, but it may be mentioned that such a "gel" is a powerful dryer, that it removes gasoline from casing-head gas, and volatile solvents from an air stream and that it removes obnoxious sulfur compounds from crude petroleum, thus suggesting the possibility of dispensing with the costly sulfuric acid treatment in refining petroleum.

The power of silica gel to adsorb sulfur dioxide and the oxides of nitrogen suggests its use in connection with the Gay-Lussac tower of a sulfuric acid plant.

Adsorbent carbon has certain advantages over silica gel, and, at present, has considerable industrial use.

The tenacity with which glass vessels retain a film of air when evacuated, even at elevated temperatures, shows us that a layer of gas molecules may be powerfully adsorbed by solid surfaces.

Fine powders "surge" when poured, and run almost like water if heated.

Each solid particle is cushioned on a film of air. We have all noticed that phosphorus pentoxide "smoke" may pass through water, an astounding fact. In this case a strongly absorbed film of air interferes with contact between the pentoxide and the water.

Carbon black, states Cabot, may occupy only five per cent of its own apparent volume, the rest being adsorbed air, and air free to move between particles.

The physical condition of the soil, its colloid content, have everything to do with its power to retain water and to hold and adsorb the fertilizing salts so vital to plant growth.

Filter colloidal ferric hydroxide through filter paper. Now attempt to filter it through a 15-cm. layer (in a 2-cm. tube) of precipitated and oven-dried silica. The spaces between grains of this fine "sand" are much larger than the pores in the filter paper, yet the sand adsorbs the colloid. Try "night blue," a dye colloidally dispersed in water.

This experiment suggests the action of sand filters in removing bacteria from city water supplies. Bacteria are organisms of colloidal dimensions.

The cleansing action of soap is in part an adsorption phenomenon. Soap in water is colloidally dispersed and so exposes great surface. It has a strong adsorptive power towards dirt, and carries dirt away on its surfaces. If soap did not adsorb dirt more strongly than does linen, for example, the dirt would remain on the linen. The older theory of cleansing action was that soap is hydrolyzed to form sodium hydroxide as needed and that the alkali does the cleaning. This is absurd, for the concentration of alkali (about 0.001 N) obtained in the hydrolysis of soap is too minute to have any value in cleansing. And alkali in any concentration has no effect in removing mineral oils. To round out the modern theory we should state that soap, by lowering the surface tension of water, emulsifies the grease or oils that so often cause the dirt to stick on the skin or fabrics and thus allows the dirt to be adsorbed by the soap and washed off. But it is to be noted that this emulsification requires rubbing to disintegrate the oil or grease.

Adsorption is relatively greater from very dilute solutions of the substance adsorbed than from more concentrated solutions and does not obey the law of definite proportions.

Adsorption may be considered a concentration of dissolved or dispersed substance upon the solid or liquid or gaseous adsorbing surface. After concentrating there the adsorbed substance may react or polymerize or dissolve or be coagulated or it may crystallize slowly.

The Gibbs Adsorption Law may be stated, "Any substance that lowers surface tension (or interfacial tension) will concentrate at interfaces."

Adsorption is generally greater from liquids of high surface tension, like water, and less from liquids of low surface tension, like alcohol. Consequently an adsorbed film of dye left by evaporation of a water solution in a glass beaker is sometimes difficult to remove completely by water but is easily removed by alcohol.

It may also be stated that a substance is adsorbed the better from liquids in which it is the least soluble (or the least peptized) granting that the liquids compared are themselves about equally adsorbed. Lundelius (Kolloid Z., 26, 145, 1920) showed this by a study of the adsorption of iodine on charcoal from CS_2, $CHCl_3$ and CCl_4.

Coagulation.—Suspensions coagulate when the causes of their stability are removed. If the colloidal aggregates coalesce and become large enough, they get beyond help from Brownian movement and settle. The destruction of protective films may lessen stability by allowing particles to coalesce. But in general the suspensoids are coagulated by addition of oppositely charged ions. The divalent ions are far more than twice as effective in precipitating power as the monovalent ions, while the trivalent ions are hundreds of times as effective. This enables us to recognize the charge on a colloid.

Test the precipitating power of 0.05 molar solutions of NaCl, Na_2SO_4 Na_2HPO_4, $BaCl_2$, and $AlCl_3$ on such typical positive and negative colloids as ferric hydroxide and arsenic sulfide. Add the salt solutions slowly. If the trivalent phosphate ion has the highest precipitating power, the colloid must be opposite in charge, namely, positive. If, on the other hand, the trivalent aluminum ion has the greatest precipitating power, the colloid must have an opposite charge, negative.

Rapid addition of an excess of a precipitating salt often carries a suspension past the precipitating point and gives it an opposite charge with a certain stability. Hardy observed that a colloid was most unstable at the ***isoelectric point.*** This point was recognized by a failure to migrate in an electric field (electrophoresis) and showed electric neutrality.

Hardy's rule of valence (Schulze's law), that the precipitating power of an electrolyte towards a given colloid depends largely upon the valence of the ion of charge opposite to that of the colloid, is useful in detecting the charge on a colloid.

Smokes and mists owe much of their stability to their electric charge and to adsorbed films of air or other gas. Hence Cottrell's high-voltage electro-precipitation method is of great use[1] in recovery of smelter fumes and acid mists.

Protective Colloids.—Mix 20 cc. of 0.1 N silver nitrate and 20 cc. of 0.1 N potassium bromide. A curdy precipitate forms. Now try the experiment again, using 20 cc. of silver nitrate to which has been added 10 cc. of 1 per cent gelatin. A suspension results when this solution is mixed with the potassium bromide solution. Gelatin is a protective colloid and forms a film around the separate particles of silver bromide so they cannot touch each other and coalesce. Gold reduced in the presence of gelatin is much more stable—harder to coagulate than without gelatin. In fact the suspensoid, or irreversible colloid particles, when covered by films of gelatin, act as if they were solid particles of gelatin—become reversible. These protective colloids are all organic compounds, hence the order to destroy all organic matter in qualitative analysis. Desired precipitations might easily be prevented by such organic matter.

About 0.4 per cent of gelatin is found in commercial ice cream. Such a product is smoother, less grainy, due to the protective effect of gelatin in preventing formation of milk sugar crystals and ice crystals. Gum arabic prevents crystallization of the sugar in marshmallows. The lactalbumen in mother's milk insures a loose, easily digested curd when the milk is coagulated by enzymes in the stomach. Cows' milk contains less of this valuable protective colloid.

Gels and Jellies.—On cooling a hot-water suspension or solution of sodium stearate soap a translucent solid called a jelly or gel results if the soap concentration is about 1 per cent or more. A 1 per cent hot gelatin solution "sets" to a jelly on cooling as does a 2 per cent agar solution. The usual "egg preserving" water glass (sodium silicate) diluted to a specific gravity of about 1.12 and then poured into an equal volume of N acetic acid sets rather soon to a slightly opaque jelly of silicic acid. When these proportions do not secure the expected result, they should be varied slightly. In the case of the water glass, if the mixture is placed in a dialyzer, at once silicic acid will pass through the membrane. Later it will not do so and still later a jelly forms.

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[1] *Ind. Eng. Chem.*, *3*, 542, 1911.

Of course these transitions can be observed only with a slow-setting gel. This shows a gradual growth in size of particle from the molecular to the colloidal.

There is some sort of a regular structure of filaments, honeycomb or flattened coalescing spheres of highly hydrated material in the aqueous jelly. Some authorities think that gels and jellies are composed of drops of a less hydrated material surrounded by a continuous mesh of more hydrated material. At any rate electrolytes and many other substances diffuse through jellies with astonishing ease.

A "brush-heap" structure of sufficiently long and slender interlacing crystals or fibers will entangle in the capillary spaces a large amount of liquid and give the appearance of a solid gel. Stirring a silicic acid jelly as it sets results in a lumpy gel. The term ***hydrated*** applies only to water systems. Jellies made from other liquids are known and they are described by the broader term ***solvated.***

The highly hydrated tissues of the body are gels. Protein is capable of swelling in water, of taking up the water, especially in the presence of a little acid or base. Accumulation of acid in the body through disease may show its effects in undue swelling (œdema) of certain tissues. Without doubt the colloid chemistry of protein is of great importance in medicine.

Fruit jellies afford a familiar example of hydrated tissues. Pectin (a carbohydrate found in most fruits), sugar, and acid (with water) are essential to the formation of fruit jellies. Color and flavor are incidental. Apples are so rich in pectin that if this constituent is lacking in a given fruit, apples or the white rind of citrus fruits may be added. When acid is lacking in the fruit, sour grapes or lemon juice are often added.

"*Solid Alcohol*" fuel may be prepared by quickly mixing about 85 volumes of 95 per cent alcohol with 15 volumes of a saturated aqueous solution of calcium acetate. The mixture "sets" to a solid jelly instantly. Cubes of it may be burned under a chafing dish. The commercial product is a cellulose ester-alcohol gel.

Soaps.—The alkali salts of oleic acid and stearic, palmitic, and the other fatty acids are the soaps we commonly use. These soaps hydrate heavily. As a result commercial soap, although sold in solid cakes, contains a surprising amount of water. Soap flakes are dryer. However, the alkali salts of the unsaturated acids, such as oleic, hydrate much less than those of the saturated acids such as palmitic and stearic. In other words, a cake of soap made from cottonseed oil (liquid unsaturated fats) contains less water than a similar cake made from hydrogenated cottonseed oil (now saturated with hydrogen). Soaps of the type of sodium oleate (*genuine* castile) disperse better in cold water than do soaps of the saturated sort, such as sodium stearate or palmitate, and therefore cleanse better at ordinary temperatures. Naturally sodium oleate is preferable for toilet use. In the very hot water of laundries sodium stearate and the rest of its class are at their best. Soaps of calcium, magnesium, lead, and of all but the alkali metals hydrate very little, do not disperse well in water, and are therefore "insoluble." They are useless for cleansing.

Froths and Films.—Adsorption films around the drops in emulsions have already been discussed. Films have, of course, but one colloidal dimension, thickness. When oleic acid, for example, dissolved in a volatile solvent, is poured on to the surface of water, it spreads, if permitted, to a film only one molecule thick.

Soap bubbles are easily blown with water solutions of the alkali soaps, but their stability depends upon the surface tension lowering caused by the soap (thus permitting great extension of surface), upon high surface viscosity and upon a low rate of evaporation. Such volatile liquids as ether do not form stable froth, although their surface tension may be very low. The thinnest spot in a soap bubble is two layers of molecules in thickness.

A film of grease is said to offer 1000 times the resistance of steel to the passage of heat. Consequently such a greasy film in a boiler causes an 8–15 per cent waste of fuel.

Mueller (Berlin) has recently prepared thin films of metal containing only 30 layers of atoms. They are transparent, and promise to be of value in scientific apparatus.

Ore Flotation.—Clean a needle in soda solution (handling with pincers.) Dry on a clean cloth. Lay on a floating tissue paper. Depress the paper gently with a stick. The paper sinks and the needle floats on the "surface skin" of the water. If greased, a larger needle can be floated. A glass rod of the same diameter, but lighter, sinks because it is easily "wetted" by water, while the steel needle is not. Grease the glass rod and it floats. Glass and steel typify the gangue and sulfide of flotation ores.

A thin glass rod that sinks in oil may be floated if first wetted by water. Flotation froths are made semi-plastic by their coating of finely powdered sulfide ore, which adheres to the oil film.

Smokes and Dusts.—In one cc. of thick smoke there may be 5,000,000 solid particles. If magnified 1,000,000,000,000 times each particle would be 0.6 cm. in diameter and placed two feet from the others.

Filtration of dust or smoke-laden air through cloth bags (bag filters in the zinc oxide industry) or, through felt or porous paper as in the gas mask is reasonably effective if the fibers are long, forming spiral paths.

Toxic smokes in warfare are hard to stop but tobacco smoke is still more difficult to catch.[1]

City fogs are persistent because of a film of soot or tarry material (from coal smoke) on the outside of each drop. This checks evaporation.

Electrical Precipitation.—The removal or recovery, from air or gases, of solid or liquid materials carried in suspension, has become one of the serious problems of industry, and one which may have several aspects. Sometimes it is a matter of purification simply—cleansing the air or gas of materials which are a waste or useless product. Sometimes it is a matter of recovering from air or waste gases materials of distinct market value.

Under the ***Cottrell process,*** the "precipitation" or removal of particles suspended in gas or air is accomplished by the use of a strong electric, or so-called static, field. An electrically charged particle in such a field tends to move—toward the negative electrode when positively charged, and toward the positive electrode when negatively charged. The suspended particles may be electrically charged in two ways: directly, when suspended in a gas which is ionized; by induction, when the gases pass through an electric field.

In electrical precipitation, it has been found that if one of the electrodes is filamentary, or has sharp points or edges, while the other electrode has a smooth and extended surface, it is possible—by impressing a high voltage across the electrodes—to ionize the gas and to cause suspended particles of solid or liquid to be precipitated upon the electrode with the smooth surface.

The electrical power consumption is merely nominal. While a high voltage is utilized, the actual current flow is so small as to be measured in milliamperes. In fact, the operation is rather more like the maintenance of a static condition than a direct and continuous flow of current. Speaking in general terms, the power consumption is 5 to 8 Kw. hours per million cubic feet of gas cleaned.

The removal of tar and other suspended impurities from manufactured gas, before it goes to the distribution system, is one of the most important problems gas engineers encounter. In 1928 the electrical precipitation plants in operation and under construction for gas cleaning totalled a treatment capacity of 520,000,000 cubic feet per day.

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[1] *Ind. Eng. Chem.*, *18*, 678, 1926.

The electrodeposition of rubber directly from the latex along with added compounding materials depends upon the negative electric charge on the rubber particles dispersed in the watery milk.

Applications of Colloid Chemistry.—All the sciences, even astronomy dealing with colloidal dust of comets' tails, are dependent on colloid chemistry for their full development.

Glues and adhesives in general are colloids, many of them of protein nature. A water-resistant glue is desperately needed in order that large timbers may be built of laminated smaller strips glued together. We can build such timbers now, but the glue ultimately weakens in moist air. With the rapid depletion of our forests this problem will become acute.

A great increase in the amount of copper and zinc recovered from their sulfide ores was secured by the flotation process. An oily froth by selective "wetting," floats the finely grouped particles of the mineral sulfides, while the waste rock, selectively "wetted" by water, sinks. Over 60,000,000 tons of ore are "floated" annually.

The productivity of a soil is closely related to its colloid content. Weathering of feldspar yields much colloidal material in the form of alumina and silicic acid. This, with colloidal hydrated oxides of iron and with humus, gives soil the proper physical condition. Humus is an indefinite mixture of organic substances, the débris of bacteria, plants, and animals. It acts as a protective colloid tending to keep much of the soil in the hydrosol state. It is opposed by the coagulating tendency of an excess of salts, by heat with drying and evaporation, and by freezing.

The tanning of leather consists essentially in making one colloid, the raw hide, insoluble by the use of another, tannin or chromium oxide. The textiles, including artificial silk, involve a detailed study of filaments, even of hydration. Dyeing is in part an adsorption of coloring matter by filaments. Rubber latex direct from the tree is a milky emulsion of rubber with a protein as the emulsifying agent. This protein is coagulated by smoking or other methods of curing. In vulcanizing raw rubber, sulfur is adsorbed.

The enormous ceramic industry deals largely with the colloidal nature of clays. To mention a single point, wet clays to be poured into molds for making heavy porcelain objects must carry a good deal of water. But in drying and baking this wet clay there is great shrinkage and distortion. Obviously if the desired fluidity could be secured with less water there would be less warping. A very little sodium hydroxide makes this possible. Adsorption of hydroxide ions peptizes the clay so that it flows as well into molds as if it contained much more water.

Cooking is a change in the colloidal structure of food. Milk itself is an emulsion. The production of food on the farm depends on the colloidal condition of the soil.

Many wheats (as California wheat, for example) yield weak gluten flours. Such gluten in the bread dough does not stretch well enough for a good loaf and admixture with a strong gluten flour is necessary. The protein of corn, rye, and other grains is "weak" in the sense that it does not permit the manufacture of a satisfactory light, porous loaf. The colloid chemist who can so change the physical condition of corn, rye, or oat protein that it will stretch like the best wheat gluten will add untold wealth to the world and have much to do with checking famines.

The alloys we use are partly suspensions of solid-in-solid. Wood, paper, clothing, glass, cement, enamels, candles, paints, varnishes, celluloid, inks, asphalt, cheese, photographic films,—these and many more are colloidal. The field is vast.

EXERCISES

1. Why do the heavy particles of red colloidal gold not sink in water?
2. How could you remove the negative charge from a negative colloid?
3. Why do some precipitates run through a filter paper on prolonged washing.
4. Give several examples of adsorption.
5. Do soap gels or silicic acid gels have definite composition?
6. How could you make an emulsion of carbon tetrachloride-in-water or of water-in-carbon tetrachloride at will?
7. How could you break an emulsion?
8. How could you distinguish between positive and negative colloids?
9. Explain the cleansing action of soap.

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CHAPTER XXXVII

METALS AND ALLOYS

METALS	NON-METALS
1. Form basic hydroxides.*	1. Form acidic hydroxides.
2. Form simple positive ions.	2. Do not form simple positive ions.
3. Reflect light well when polished.	3. Do not usually show "metallic luster."
4. Conduct electricty and heat well.	4. Do not conduct heat and electricity well.
5. As a class are malleable and ductile.	5. In general are not malleable or ductile.

* There are a few elements, such as aluminum, whose hydroxides yield both hydrogen and hydroxyl ions.

METALS

Metals are valued for such physical properties as malleability, tenacity, conductivity, and luster.

Iron can be rolled into suitable shapes when red hot. Zinc is most readily rolled at 100°–150° and is actually brittle at 205°. Gold leaf has been hammered to a thickness of 0.0001 mm. Lead is far from ductile, while platinum wire has been drawn to a diameter of 0.00008 mm., and 1 gram of gold can be drawn into a wire 3,240 meters in length.

Any metal or alloy obtainable in wire can be sprayed. The spraying tool, weighing three pounds, contains a feeding mechanism, driven by compressed air, which feeds the metal wire automatically towards the tip of a nozzle, where it is melted by an oxygen-acetylene flame. As soon as a drop of metal forms, it is instantly atomized by compressed air and impacted upon the surface to be coated. Metal coatings can thus be formed on practically any clean surface.

These metal coatings can be built up to any desired thickness, from 1/1000th of an inch up to an inch or more. Such coatings are applied for ornamental purposes and as a protection against rust.

It is a fortunate thing that copper with unusually high electrical conductivity is reasonably plentiful and cheap. It is also fortunate that mercury is liquid at ordinary temperatures, is rather inactive chemically, and is a conductor of heat and electricity. If it lacked in any of these properties we would do without some very important scientific instruments.

Metals dissolve in each other, to some extent, forming alloys; and yet some alloys are real compounds of the metals. Alloys are more fully discussed on page 477.

Occurrence.—The least active metals, such as gold, silver, and copper, occur free in nature. *Oxides*, as those of iron, zinc, aluminum, are common ores. There are many *sulfide* ores, notably those of copper, zinc, and lead, to which may be added iron pyrites. Copper, zinc, iron, and lead are found as *carbonates*, as are barium, calcium, and strontium. *Silicates* are very common but are used in ceramics (in the form of clays and feldspar) rather than as sources of metals.

Extraction from the Ores.—When a metal occurs free in an ore it can usually be melted away from the rock.

Oxides are usually reduced by hot coke or by carbon monoxide as in the process of making pig iron. Oxides may also be reduced by ignited aluminum powder (Goldschmidt process).

$$3\ Mn_3O_4 + 8\ Al \longrightarrow 4\ Al_2O_3 + 9\ Mn.$$

Carbonates and hydroxides are converted into oxides by roasting and are then reduced to metal by hot coke. Roasted sulfides yield sulfur dioxide and the oxide of the metal.

Electrolysis of their fused hydroxides now furnishes us with sodium and potassium although magnesium and calcium are now prepared by electrolysis of their fused salts. A solution of aluminum oxide in melted fluorides is electrolyzed to produce aluminum.

Preparation of Metallic Compounds.—Oxides are prepared by direct union of the elements, usually at high temperatures, and by heating hydroxides, carbonates, or most nitrates.

Hydroxides are secured by union of a metallic oxide with water or by double decomposition between a soluble base and a salt of the metal concerned.

The preparation of salts was discussed on page 186. In addition it may be observed that sulfates are reduced to sulfides by reduction with hot carbon. When acidic and basic anhydrides are fused together salts result.

$$CaO + SiO_2 \longrightarrow CaSiO_3.$$

MELTING POINTS *		DENSITIES	
Carbon	3600°C	Gold	19.32
Tungsten	3400°	Lead	11.34
Chromium	1615°	Copper	8.93
Iron	1530°	Iron	7.86
Aluminum	658.7°	Tin	7.30
Zinc	419.4°	Zinc	7.10
Lead	327.4°	Aluminum	2.70
Phosphorus	44.0°	Magnesium	1.74

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* Carbon and phosphorus in this list are non-metals but the comparison of melting points is interesting.

Expansion Coefficients.—The rate at which a metal or alloy expands with rise in temperature is important. Beryllium, for example, has the same coefficient of expansion as cast iron, hence if used (when cheaper!) for light pistons inside the iron cylinders of automobile engines it will present far less engineering difficulty than do other light pistons which expand at a rate different from that of iron.

COEFFICIENTS OF THERMAL EXPANSION

Iron	0.000,012,1	Glass (Jena)	0.000,005,70
Nickel	0.000,012,8	Glass Pyrex	0.000,003,20
Nickel Steel	0.000,000,90	Silica (fused)	0.000,000,54
Platinum	0.000,008,99 at 40°		

The above table indicates the proper choice of wires to be fused into glass tubes or used in reinforcing sheets of glass. Unless both solids have nearly the same coefficients of expansion, cracking of glass results.

The Crystal Structure of Metals.—The most common metals crystallize in three simple lattice types. The more ductile metals, such as gold, silver, copper, and aluminum, belong to the face-centered cubic lattice type. Less ductile metals, such as molybdenum, tungsten, and chromium, belong to the body-centered lattice type, in which the face-centered atoms of the unit cube are replaced by a single atom at the cube center. (Page 67.)

The element iron crystallizes in the body-centered lattice at room temperature and has a face-centered cubic allotropic modification above 900° C. The third common lattice type is the hexagonal, in which such elements as zinc, magnesium, and cadmium crystallize.

When metals are mechanically worked there may be a slipping along certain crystal planes with development of hardness by slip interference.

Alloys

Centuries ago pure metals were practically unknown. In the metallurgy of copper, for example, other metals present in the ore mixed with the copper to form an alloy. We are told of the "lost art" of hardening copper and yet the explanation is simple. Certain copper ores containing other metals yielded alloys much harder than pure copper. Then metal workers learned that addition of some copper to gold or silver in coins made a product that was much harder and therefore lasted longer. In ancient times copper and zinc were alloyed to form brass and copper with tin to form bronze. Alloys have multiplied greatly, but it is only recently that their preparation and study have become genuinely scientific. Here is a field of dazzling promise, only partly explored as yet.

It has recently been found that electrolysis of melted alloys is possible. During electrolysis of a sodium-potassium alloy the potassium migrates to the cathode and the sodium to the anode. Evidently the highly electropositive sodium becomes relatively negative when combined with the still more positive potassium.

"Lead melts at 327 degrees C., but when antimony is dissolved in the molten metal the freezing point of the lead is lowered, just as the freezing point of water is lowered by dissolved substances. Antimony melts at 630 degrees C. and the addition of lead to melted antimony also lowers its freezing point. If a curve is drawn showing the temperature where the lead just commences to solidify (or the temperature of its complete melting) as antimony is added, and if from the other side of the diagram a similar curve is drawn showing the lowering of the freezing temperature of the antimony as lead is added, these two curves will meet in a point, and the temperature and the composition represented by this point on the diagram will indicate the melting point and percentage composition of the lowest melting alloy of the series.

"This lowest melting alloy represented by the point E has a definite melting point (248° C.) and a definite composition (87.5 per cent lead) and is called the *eutectic* of the series" (*American Magnesium Corporation*).

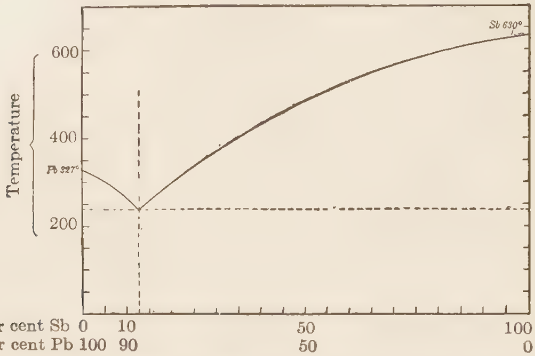

FIG. 135.—Melting point curves of varying mixtures of lead and antimony.

Alloys are of at least four main types:

1. A solid solution of one metal in another, or in several others.
2. A definite chemical compound of two or more metals.
3. A mixture of such a compound with an excess of either constituent. This means particles of the compound in a matrix of the rest of the material.
4. A mixture of a solid solution with an excess of either constituent. Again we have solid particles (the solid solution) in a matrix of the rest of the material.

Alloys are usually made by melting the constituents together, although there are other ways. On cooling, solid particles of one type may separate from the uniform molten mixture. When a polished surface of such an alloy is etched by a suitable chemical and examined under the microscope, the shape and arrangement of these crystals or aggregates is clearly seen. Such a study is called "metallography."

Microscopic examination shows that metals and alloys are rather complex in structure, that they are built up of aggregates of crystalline grains. The strength and other physical properties of alloys depend to a marked extent on the arrangement of these grains.

The "antifriction" or bearing metals which surround revolving shafts are interesting examples of the separation of solid particles in the matrix. These "Babbitts," as they are often called, are alloys of tin and antimony, with some lead and copper. A surface of the harder particles stands the wear and these in turn are supported by a softer matrix into which they sink. In an alloy of a hard matrix and softer separate aggregates scattered through the mass the heat developed by friction is much greater.

The low-melting alloys, such as Wood's metal or Rose's metal, have an important application. The automatic sprinklers dotting the ceilings of great department stores or factories are merely water pipes closed by a plug of such an alloy. When a fire starts these plugs melt very soon and release a spray of water. Wood's metal melts at 60.5°. Solder is another low-melting alloy of value. Each metal in the solid solution lowers the melting point or freezing point of the others, hence the mixture melts at a lower temperature than the constituents. This is the same as with salt in water.

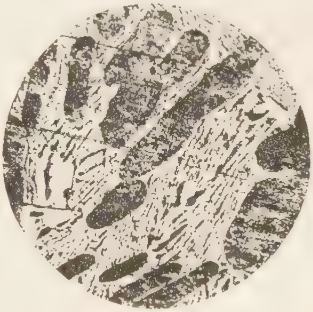

Fig. 136.—Alloy of 40 per cent Bi and 60 per cent Cd (× 125). Black masses are Cd crystals in the eutectic mixture of 62 per cent Bi and 38 per cent Cd which melts at about 150° C.

Aluminum bronze (copper and aluminum with possibly a little of some other elements) has the appearance of gold, yet is hard, machines well, and is not easily corroded. Duralumin, the strongest of the light-weight alloys, essential for the rigid framework of airships, can be cast sharply and has strength approaching that of steel, which unfortunately does not cast sharply and must be machined at greater expense.

Iron alloys of the utmost importance in steel making will be discussed under Iron and Steel.

Amalgams are alloys with mercury as one constituent. Silver amalgam is used in filling teeth.

Plumber's solder (2 parts lead to one of tin) does not change suddenly from liquid to solid on cooling, but freezes slowly through a certain temperature range. The formation of lead-rich crystals carried in melted metal produces the pasty condition that makes possible the plumber's "wiped joint."

Many inter-metallic compounds are hard, brittle and lacking in ductility and strength.

COMPOSITION AND USES OF ALLOYS[1]

NAME	PER CENT COMPOSITION	USES
Aluminum Brass	Cu 68–70 Zn 27–31 Al 1–3	Propeller blades, rudder frames, sea valves
Brass	Cu 73–66 Zn 27–34	Sheets, tubes, cartridges, etc.
Bronze	Cu 88 Sn 8 Zn 2 Pb 2	Strong valves and fittings.
Bronze (aluminum)	Cu 90 Al 10	Hard, non-corrodible, ornamental.
Babbitt metal	Sn 70–90 Sb 7–24 Cu 2–22	Bearings.
Bell metal	Cu 80–75 Sn 20–25	Bells, gongs.
Brittannia metal	Sn 95–90 Sb 5–10 Cu 1–3	Cheap table ware.
Chromel (Nichrome)	Ni 60 Cr 40	Resistance wire for electric heating. (Patented.)
Duralumin	Al 95.5 Cu 3.0 Mn 1.0 Mg 0.5	Strongest and best of aluminum alloys. Airplane and auto parts.
Fusible (Wood's)	Bi 38 Pb 31 Sn 15 Cd 16	Automatic sprinklers, fuse plugs.
German silver	Ni 18–25 Zn 20–30 Cu (remainder)	Table ware, cheap jewelry.
Gold (White) (1)	Au 82 Ni 18	Jewelry.
Gold (White) (2)	Au 90 Pd 10	
Invar	Fe 64 Ni 36	Low coefficient of expansion. Used in precision instruments, clocks, etc

If aluminum and silicon (5 to 15 per cent) are melted together and then treated with sodium or sodium fluoride the alloy structure is "modified" with great increase in tensile strength and elongation under stress as well as adaptability to casting.

Aluminum alloy pistons are valuable because of their great heat conductivity, which cools the motor.

Bearing Metals.—" The first significant fact observed in the study of bearing metals is that not a single pure homogeneous metal has given satisfactory service; all bearing metals are alloys made up of two or more phases—that is, they consist of hard and

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[1] From *Principles of Metallography* by Williams. Published by McGraw-Hill and Co., New York.

Composition and Uses of Alloys—*Continued*

Name	Per Cent Composition	Uses
Magnalium	Al 90–94 Mg 10–6	Scientific instruments. Balance beams.
Manganese bronze	Cu 56 Zn 41 Sn 0.5 Fe 1.0 Mn 0.5 Al 1.0	Propeller blades, non-corrodible and with great wearing qualities.
Monel metal	Ni 72 Cu 26.5 Fe 1.5	Almost non-corrodible. Propeller blades, wire, sheets, etc.
Palau	Pd Au	Substitute for Pt in chemical crucibles, dishes, etc.
Pewter	Sn 85–90 Sb 15–10	Platters, bowls, cups, etc. Little used at present.
Platinate	Fe 54 Ni 46 C 0.15	Same coefficient of expansion as glass. Substitute for Pt in incandescent lamps.
Solder (soft)	Pb 67 Sn 33	Plumbers' solder.
Steel (low carbon)	C 0.05–0.25 Fe (remainder)	Boiler plate, rivets, sheet, structural work, bridges, shafting.
Steel (medium carbon)	C 0.4–0.8	
Steel (high carbon)	C 1.2–1.5	Cutlery, rails, wood-working tools, drills, castings. Saws, files, razors, ball bearings.
Stellite	Co 80–50 Cr 20–50 W ?	Non-corrodible. Used in high-speed tools, cutlery, surgical instruments. (Patented.)
Type metal	Pb 60–85 Sb 8–20 Sn 5–35	Printers' type.

relatively soft microscopic particles intimately mixed. The function of the hard particles, or ***bearing crystals,*** is to support the load and resist the wear when actual metallic contact exists between the bearing surfaces. The functions of the softer particles are to allow the harder particles to adjust themselves to the surface requirements of the journal and to wear down slightly below the surface of the harder, forming slight depressions on the apparently smooth wearing surface of the bearing, in which some of the lubricant is held when the bearing surfaces are brought into contact with each other. It is this characteristic of certain alloys to form these slight depressions, and thus provide the means for retaining a lubricant, that characterizes them as true bearing metals; in fact, a bearing metal has been defined as bearing metal

"an alloy that is capable of retaining a lubricant upon a bearing surface." The extent to which the lubricant can be so held determines the most valuable characteristic of an alloy as a bearing metal." (C. H. Bierbaum.)

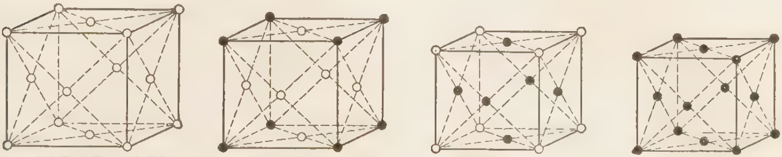
Solid Solutions of Metals.—On cooling an alloy of copper-zinc, crystals of nearly pure copper form first, followed by formation of crystals gradually becoming richer in zinc. In the solid form this alloy is an aggregate of grains with a zinc content varying from center to outer layer of the mass. Now on prolonged heating at about 800° C. diffusion renders the alloy chemically homogeneous. Mechanical working has a somewhat similar influence as the annealing.

After allowing time for such diffusion the brasses are then homogeneous up to 36 per cent zinc. Examined with the X-ray spectrometer, these alloys show only one pattern, that of the face-centered cubic lattice characteristic of pure copper, although zinc, itself hexagonal in crystal structure, may be present to the extent of over 30 per cent. Evidently these zinc atoms occupy the positions of some of the copper atoms in the face-centered cubic lattice (Jeffries and Archer).

When two metals form a solid solution both the hardness and the electrical resistance are increased by adding either metal to the other, up to a maximum at about an equality in number of atoms. All of the electrical resistance wires ("heating elements") on the market are solid solutions. The decrease in resistance of a pure metal with fall in temperature is due to improved contact between atoms, making the passage of electrons from atom to atom easier.

Bridgeman believes that when the atoms of two metals enter side by side into the same crystal lattice as in solid solutions there must be some degree of resemblance in the two kinds of atoms. The resemblance is not complete, however, and the indiscriminate use of either kind of atom in the crystal lattice is possible only with a certain amount of distortion. The consequent imperfect fitting between adjacent atoms offers some difficulty to the passage of electrons from atom to atom, to the flow of electricity.

Gold and copper mix in all proportions like alcohol and water, because the atoms of one fit easily into the crystal space lattice of the other. The series of solid solutions remains face-centered cubic throughout (X-ray evidence). There is, in fact, a slight stretching of the copper lattice by substitution of gold atoms, but this is modified by the fact that unlike atoms of metals attract one another more closely than like ones.



100 Per Cent Gold

75 Per Cent Gold
25 Per Cent Copper

25 Per Cent Gold
75 Per Cent Copper

100 Per Cent Copper

FIG. 137.—The crystal lattice structure of gold-copper alloys.

EXERCISES

1. If we had no alloys and had to depend upon practically pure metals, what difference would it make in our daily life?

2. Aluminum melts at 659° and antimony at 630° but a certain alloy of the two metals melts at 1,066°. How can this be?

<— * NaOH + NCl

CHAPTER XXXVIII

THE ALKALI METALS

Element	Atomic Weight	Density	Melting Point	Boiling Point	Atomic Volume = At. Wt. / Density
Lithium.....(Li)	6.94	0.534	186.0°	1400.0°	13.1
Sodium.....(Na)	23.00	0.971	97.0°	877.5°	23.7
Potassium...(K)	39.10	0.862	62.5°	700.0°	45.4
Rubidium...(Rb)	85.45	1.532	38.5°	696.0°	55.8
Cæsium.....(Cs)	132.81	1.87	26.5°	670.0°	71.0

This group of elements, as shown by its position in the periodic system, is strongly metallic. The alkali metals are the most active of all metals, reacting violently with water, and hence are not found free in nature. In the laboratory these metals must be kept under oil to exclude moisture and oxygen. Their hydroxides are the strongest bases. The elements are soft with a silvery luster, quickly tarnishing in the air with formation of layers of oxide, hydroxide, and carbonate. All the elements of this group are obtained by electrolysis of their fused salts or hydroxides or by reduction of oxides, carbonates, or hydroxides. The valence is uniformly one throughout the group.

In some respects lithium is different from the rest of the group, but in general, density, melting point, and other properties change regularly with atomic weights within the group. Nearly all the salts are white and very few are insoluble. For most uses the cheaper sodium compounds can be substituted for potassium compounds.

The hypothetical metal, ammonium (NH_4), in a way belongs to this group, although it is known only in combination.

Exercise 1.—If you should discover a new metal, monovalent and strongly base-forming, with atomic weight about 224, what would be its approximate density, melting point, boiling point, and atomic volume?

Lithium

Lithium is far from plentiful and its compounds have few uses. It is the lightest solid known (except frozen hydrogen) and one of the most active metals. Lithium unites with nitrogen at ordinary temperatures:

$$6\ Li + N_2 \longrightarrow 2\ Li_3N.$$

The glass industry is using lithium minerals (lepidolite and spodumene) found in New Mexico to toughen translucent glassware. With larger amounts lepidolite is a good substitute for fluorspar in the manufacture of white opaque glass and enamels.

SODIUM

The occurrence, preparation, and properties of sodium were discussed on pages 195–196.

Sodium Chloride.—Fortunately for the human race this necessary mineral is plentiful in most countries. Two thirds of the solid in sea water is common salt, and some is still obtained from this source by solar evaporation. The ocean carries over 3 per cent solids and Great Salt Lake more than 20 per cent. Great beds of solid salt are found at Stassfurt, at Salzburg, and in several districts of the United States. Dried-up lakes have left easily mined deposits. Deep beds are usually tapped with wells and, if necessary, water introduced to form a brine. This brine, or any natural brine, is pumped up and concentrated. Some brines

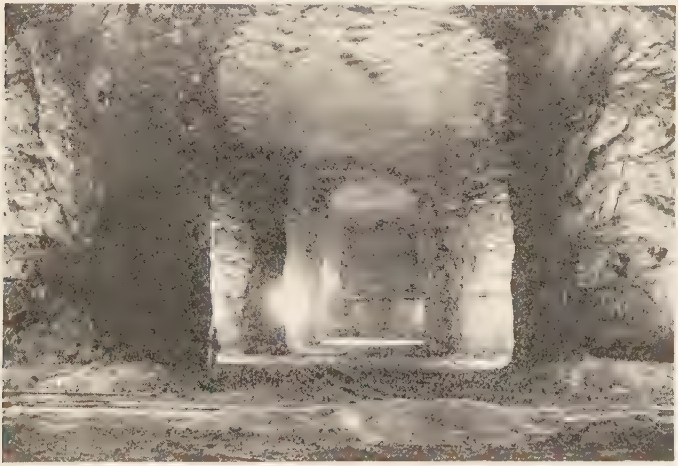


FIG. 138.—A salt mine in Louisiana.

contain magnesium chloride and bromide. On too great concentration these begin to crystallize from the "bitter liquor." As a rule this bitter water is electrolyzed so as to release only the bromine (see page 170). Some magnesium chloride contaminates table salt. It is this very soluble and hygroscopic impurity that makes salt "cake" in the table shakers. Starch is often added to coat each particle. Baking soda ($NaHCO_3$) is used also to convert the magnesium chloride into the insoluble carbonate.

Salt crystallizes in cubes with hollow faces. It melts at 803° and volatilizes at high temperatures. As the chief source of sodium compounds, as a food preservative, and as an essential article of diet sodium chloride is of major importance. It is startling to learn that the average man eats 29 pounds of salt yearly in his food.

The United States alone produces 7,700,000 tons of salt yearly. The great producing states are New York, Michigan, Ohio, Kansas, Louisiana, California, Texas, Utah, and West Virginia.

Over a thousand feet below the city of Detroit salt is mined to the extent of 1500 tons every day.

Sodium Bromide and Sodium Iodide.—These salts resemble the chloride in many respects. Both are used in medicine and in photography. They are prepared by the action of bromine or iodine on sodium hydroxide or by adding sodium carbonate to a mixture of iron filings and the free halogen.

Sodium Fluoride.—This compound differs from the chloride, bromide, and iodide in being only moderately soluble. It has a use as a preservative in distilleries, yeast factories, and in checking decay of wood.

Sodium hydroxide was discussed on pages 196–198.

Sodium Carbonate, or Sal Soda, Na_2CO_3.—There are a few matural deposits of "soda," notably the one in British East Africa, where Lake Magadi rests upon ninety square miles of crystallized sodium carbonate. This Magadi deposit is now being worked. Smaller soda lakes are found in California, Oregon, and British Columbia. Before 1791 practically all of this salt used was obtained from the ashes of sea plants (inland plants yield potassium carbonate on burning). Naturally sodium carbonate was expensive and, as a result, so were glass and soap. It is scarcely an exaggeration to say that the progress of civilization was greatly retarded for want of a cheap source of sodium carbonate. During the Napoleonic wars France was deprived of its usual supply, so Napoleon offered a prize of 100,000 francs for the discovery of a method for manufacturing an adequate supply from common salt. Le Blanc rose to the occasion.

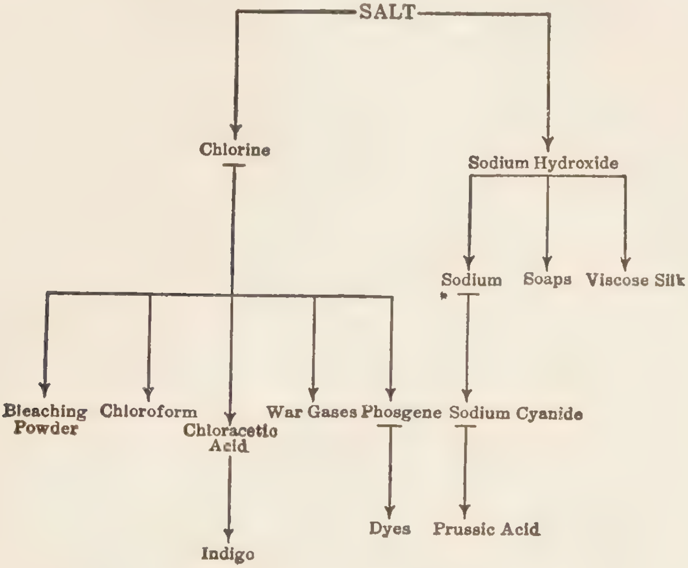

SALT
Chlorine
Sodium Hydroxide
Sodium
Soaps
Viscose Silk
Bleaching Powder
Chloroform
Chloracetic Acid
War Gases
Phosgene
Sodium Cyanide
Dyes
Prussic Acid
Indigo

FIG. 139.—Products from salt.

The LeBlanc Process. In this once famous but now obsolete process, sodium chloride was heated with concentrated sulfuric acid to form sodium sulfate and the useful hydrogen chloride as a by-product.

Reduction of the sodium sulfate to the sulfide by hot carbon then followed. Reaction of this sodium sulfide with calcium carbonate completed the process with formation of sodium carbonate which was finally washed out of the mixture with water. The process competed for a time with the Solvay process, because of the sale of the hydrochloric acid by-product, but now LeBlanc plants are no longer built.

The Solvay Process. The Le Blanc method had no rival until 1863, when the Belgians, Ernest and Alfred Solvay, achieved success with their ammonia-soda process. Concentrated sodium chloride solution is saturated with ammonia and carbon dioxide. At first ammonium bicarbonate, $(NH_4)HCO_3$, is formed and this reacts with sodium chloride to form sodium bicarbonate. The latter salt, only sparingly soluble in the salt solution, precipitates, and after removal is heated to form sodium carbonate:

$$\begin{aligned} NH_4OH + H_2CO_3 &\longrightarrow (NH_4)HCO_3 + H_2O, \\ (NH_4)HCO_3 + NaCl &\longrightarrow NaHCO_3 + NH_4Cl, \\ 2\ NaHCO_3 &\longrightarrow Na_2CO_3 + H_2O + CO_2. \end{aligned}$$

The process is carried on in steel towers about 50 feet high and 6 feet wide with numerous shelves and water traps to insure thorough mixing. The gases are led in at the bottom and halfway up the side. The temperature in these carbonating towers should not rise above 35° C.

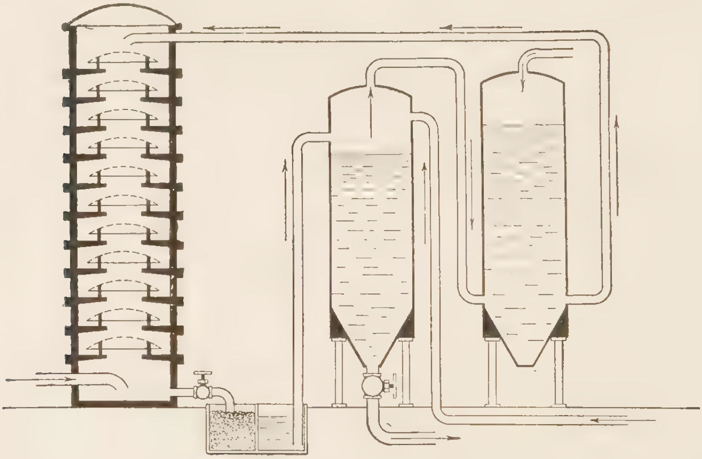


FIG. 140.—Solvay soda process. The ammonium chloride solution from the tower is pumped into a cylinder where it is mixed with lime water. The escaping ammonia is led into a cylinder of salt brine which is then pumped into the carbonating tower.

The economy of operation is great. Instead of wasting the ammonium chloride produced it is heated with lime to release ammonia gas, which, of course, is passed into the towers again. And instead of buying this necessary lime in the open market it is made at the plant by heating limestone to about 900°. The carbon dioxide released from the calcium carbonate is used in the carbonating tower:

$$\begin{aligned} CaCO_3 &\longrightarrow CaO + CO_2, \\ Ca(OH)_2 + 2\ NH_4Cl &\longrightarrow CaCl_2 + 2\ NH_3 + 2\ H_2O. \end{aligned}$$

There is only one thing to mar perfection of economy. The calcium chloride by-product finds a very poor market. The consumption of fuel is much less than in the Le Blanc process and the product is purer.

There is no question of the superior efficiency of the Solvay method, and the Le Blanc process would long ago have been discarded but for the value of its by-product, hydrochloric acid. As it is, practically all of the world's soda is Solvay soda. It is possible that the Haber process for making ammonia will be operated in connection with the Solvay process for making soda.

The normal annual production in the United States is about 1,500,000 tons of soda. It is essential to many important industries, such as the manufacture of glass, soap, paper, leather, enamels. It is also used in cleansing, water softening, dyeing, and oil refining.

Exercise 2.—Draw a sodium carbonate tree, root and branch, like the oxygen tree on page 37.

Sodium carbonate is a white solid, very soluble in water, yielding alkaline solutions by hydrolysis. On concentrating these solutions various hydrates crystallize according to the temperature. On standing in the air the decahydrate effloresces, due to its high vapor tension, and crumbles to a white powder, which is the monohydrate. For some purposes the decahydrate is liked because it dissolves more rapidly. The common names for sodium carbonate are washing soda and sal soda.

Distribution of Sodium Carbonate in the United States, 1929

	Tons
Glass	672,000
Soap	213,000
Chemicals	335,000
Cleansers	125,000
Pulp and paper	110,000
Water softeners	60,000
Textiles	40,000
Petroleum refining	26,000
Exports	40,000
Miscellaneous	47,000
Total	1,668,000

Statistics for *sodium hydroxide* are given on page 198.

Sodium Bicarbonate, $NaHCO_3$.—This so-called baking soda is the direct product of the Solvay process. About one ton out of every seven is sold in that form to be used in baking powders, in medicine, etc. The rest is heated to secure the normal carbonate:

$$2\ NaHCO_3 \longrightarrow H_2O + CO_2 + Na_2CO_3.$$

Although Na_2CO_3 solutions are strongly alkaline by hydrolysis, $NaHCO_3$ solutions are neutral to phenolphthalein. Since the latter solutions are perceptibly alkaline to methyl orange, there is really a slight excess of OH^- ions present. But the amount of hydrolysis is small in comparison with that in sodium carbonate solutions. From the formula the student may expect hydrogen ions, but the HCO_3 ion is very stable.

Exercise 3.—Represent by equations the hydrolysis of sodium carbonate

Baking Powders.—To secure plenty of surface in dough, thus making the product "light," some gas must be released throughout the mixture. Air would do, but it is more convenient to have carbon dioxide released. This can be accomplished by addition of a harmless acid (or acid salt) to baking soda. Lactic acid of sour milk has been used with uncertain results when the amount added was not exactly equivalent to the soda. Cream of tartar baking powders serve the purpose very well. They are mixtures of acid potassium tartrate and sodium bicarbonate. The hydrogen ions from the acid salt unite with the HCO_3 ions from the sodium bicarbonate to form carbonic acid, which breaks down into water and carbon dioxide:

$$H^+ + HCO_3^- \rightarrow H_2CO_3.$$

Phosphate baking powders contain an acid phosphate. "Alum" baking powders depend upon the acid reaction caused by hydrolysis in alum solutions. As a matter of fact common alum is not used but instead, anhydrous aluminum sulfate. This, however, makes no difference in the physiological effects which are probably negligible. With all these the salts left in the food are harmless unless used in excessive quantities.

The phosphate-alum type is the most popular. A phosphate powder in the cold is rapid enough and progressive enough to prepare the dough for the oven while the more slowly soluble alum keeps the carbon dioxide evolving until the dough is set by heat.

A cream of tartar powder gives off its carbon dioxide too well in the early part of the operation, so jarring or slow baking may spoil things.

Lecture Experiment.—If to concentrated ammonia water, saturated with sodium chloride a lump of solid carbon dioxide is added, a copious precipitate of sodium bicarbonate is obtained in ten minutes. The experiment works best in a 2-inch cylinder, about half-filled.

Sodium Sulfate, Na_2SO_4.—Unlimited quantities of this salt are found in Siberian lakes and in a bay of the Caspian Sea, and great deposits fully 98 per cent pure are located in the southwestern part of the United States. Glauber, the alchemist, used it in medicine as early as the middle of the seventeenth century, hence the name Glauber's salt. It crystallizes below 32.38° as $Na_2SO_4 \cdot 10\ H_2O$ and above this transition point as the anhydrous salt, Na_2SO_4. This transition temperature is so definitely marked that it has been used in calibrating thermometers. Considerable quantities are used in glass making and in making paper from certain woods such as southern pine. Our annual needs for this and for the dye industry total nearly 400,000 tons. At Stassfurt the magnesium sulfate obtained as a by-product in separating potassium chloride is mixed with a solution of sodium chloride:

$$MgSO_4 + 2\ NaCl \longrightarrow MgCl_2 + Na_2SO_4.$$

The sodium sulfate is the least soluble of the four salts and crystallizes out.

Sodium Sulfite, Na_2SO_3.—The sulfite of sodium is obtained by saturating a solution of the carbonate with sulfur dioxide and then adding an amount of the carbonate just equal to that taken at first:

$$(1)\quad Na_2CO_3 + 2\ H_2SO_3 \longrightarrow H_2CO_3 + 2\ NaHSO_3,$$
$$(2)\quad Na_2CO_3 + 2\ NaHSO_3 \longrightarrow H_2CO_3 + 2\ Na_2SO_3.$$

It is used in photography and as an *antichlor* in the textile industry. Chlorine left in the fabric after bleaching weakens the fibers, but if sodium sulfite is added the chlorine reacts to form harmless salt. Sulfites readily oxidize in the air, so they are apt to be contaminated with sulfate. They are good reducing agents.

Sodium bisulfite, $NaHSO_3$, is the product of reaction (1). It is used in paper making, chrome tanning, making dyestuffs, and as an antichlor.

Sodium Thiosulfate, $Na_2S_2O_3$.—Photographers know this compound as "hypo" and use it to dissolve unused silver bromide from the developed plates. It is formed very easily by boiling sodium sulfite with sulfur:

$$Na_2SO_3 + S \longrightarrow Na_2S_2O_3.$$

On acidifying a solution of sodium thiosulfate the acid of which it is a salt is liberated. In other words thiosulfuric acid is set free. This acid is very unstable, breaking down at once into free sulfur and sulfurous acid, which is also unstable:

$$\begin{array}{ll} (1) & Na_2S_2O_3 + 2\ HCl \longrightarrow 2\ NaCl + H_2S_2O_3, \\ (2) & H_2S_2O_3 \longrightarrow H_2SO_3 + S, \\ (3) & H_2SO_3 \longrightarrow H_2O + SO_2. \end{array}$$

The salt is used in quantitative determination of free iodine because it reacts with iodine to form colorless compounds, sodium iodide and sodium tetrathionate:

$$2\ Na_2S_2O_3 + I_2 \longrightarrow 2\ NaI + Na_2S_4O_6.$$

Exercise 4.—If a solution of iodine in potassium iodide is added to sodium thiosulfate, what color change takes place? Write the equations.

Sodium Sulfide, Na_2S.—The laboratory preparation consists in dividing any solution of sodium hydroxide into two equal parts, saturating one with hydrogen sulfide and mixing the two portions:

$$\begin{array}{ll} (1) & NaOH + H_2S \longrightarrow NaHS + H_2O, \\ (2) & NaOH + NaHS \longrightarrow Na_2S + H_2O. \end{array}$$

Commercial reduction of sodium sulfate with carbon at 900° also yields sodium sulfide which is also a by-product of the barium sulfate industry. It is a very soluble crystalline salt. In solution it is strongly basic, due to hydrolysis, since it is a salt of a strong base and a weak acid. It is a necessary aid to the "sulfur colors" in dyeing cotton and is also required in the manufacture of certain dyes. Its solution removes hair from hides and denitrates artificial silk. When a sodium sulfide solution is heated with sulfur, certain polysulfides of sodium are formed.

Sodium Cyanide, NaCN.—The Bucher process of making available the free nitrogen of air was once used in production of sodium cyanide. With iron, or iron oxide promoted by sodium fluoride as a catalyst, a reaction takes place between hot soda ash, powdered coal, and nitrogen of the air or of producer gas:

$$Na_2CO_3 + 4\ C + N_2 \longrightarrow 2\ NaCN + 3\ CO.$$

A more common method involves the fusion of cyanamide (p. 321) with carbon and sodium carbonate.

$$CaCN_2 + C + Na_2CO_3 \longrightarrow CaCO_3 + 2\ NaCN.$$

It is important to produce cheap sodium cyanide because it is much used in extracting gold from low-grade ores. A cheap product, good enough for gold extraction, is prepared by heating cyanamide with salt. Prussic acid, HCN, which is released on acidifying the cyanide, is largely used in the fumigation of fruit trees. More cyanide is used for this purpose than for metallurgy. Cyanides are important in electroplating, case-hardening of steel, and as a fluxing material. We import 33,000,000 pounds yearly. All the cyanides are extremely poisonous.

Sodium Nitrate, $NaNO_3$.—This salt has been discussed in previous chapters in connection with nitric acid and fertilizers. The largest deposit is in the dry region of northern Chile, but a few unimportant deposits occur elsewhere. The crude "caliche" is purified by recrystallization from water. It is used somewhat in the cheapest gunpowder, but is too deliquescent for the purpose. Potassium nitrate is preferred. Chilean production, now dwindling from competition with synthetic ammonia, is about 3,000,000 tons.

Sodium Nitrite, $NaNO_2$.—The nitrite is made by heating the nitrate. Loss of oxygen is expedited by heating with lead. The lead oxide formed is separated by filtration from the soluble nitrite:

$$2\,NaNO_3 \longrightarrow 2\,NaNO_2 + O_2,$$
$$NaNO_3 + Pb \longrightarrow NaNO_2 + PbO.$$

Most of it is produced by passing oxides of nitrogen (from the electric arc) into a solution of sodium hydroxide. The United States uses about 4000 tons of the nitrite annually in the manufacture of dyes.

It has long been the custom to add either potassium nitrate (saltpeter) or sodium nitrate to pickled meats for the sake of the improved color. It now appears that the nitrates are reduced to nitrites in the pickle solution, so sodium nitrite is being substituted, using only one-tenth as much by weight.

EXERCISE 5.—From Chapter XX learn the method of detecting the difference between a nitrate and a nitrite.

EXERCISE 6.—What are the reactions involved in the electric arc process of making sodium nitrite?

The Sodium Phosphates.—There are three phosphates of sodium: NaH_2PO_4 of nearly neutral reaction in water; Na_2HPO_4 of faintly basic reaction; and Na_3PO_4 of strongly basic reaction.

These are prepared by adding proper amounts of sodium hydroxide to orthophosphoric acid.

Sodium Perborate, $Na_2B_4O_8 \cdot 10H_2O$.—The perborate is prepared by adding borax to a solution of sodium carbonate while it is being electrolyzed. It is a useful bleaching agent yielding hydrogen peroxide in water for the laundry.

Tests for Sodium Compounds.—There are no insoluble sodium salts except sodium uranyl acetate, the fluosilicate and the pyroantimonate, $Na_2H_2Sb_2O_7$. Addition of the soluble potassium pyroantimonate to a solution of a sodium salt yields the latter compound as a precipitate. Sodium salts are recognized by the intense yellow color they give to a colorless flame. The test is too delicate, for even the dust of the air colors a flame yellow. As a rule we report sodium in qualitative analysis only for very intense and prolonged coloration of the flame. With the spectroscope the element is recognized by characteristic yellow lines.

A remarkably delicate precipitation test for sodium was described by Kolthoff.[1] By using zinc uranyl acetate as reagent 0.1 g. sodium can be detected in the presence of 100 g. of potassium. It aids the delicacy of the test if excessive amounts of potassium salts are first removed by precipitation with a solution of ammonium perchlorate in 70 per cent alcohol. It has also been suggested that a solution of cobalt uranyl acetate in normal acetic acid gives a better sodium precipitation than does the zinc uranyl acetate.

Ten cc. of a uranyl zinc acetate solution prepared by dissolving 4 grams of uranyl acetate and 15 grams of zinc acetate in 50 cc. of water acidified with 1 cc. of glacial acetic acid, will precipitate completely 8 mg. of sodium, if present, from 1 cc. of a solution of sodium salts in 1 hour. This ratio of 10 cc. reagent to 1 cc. of test solution must be used.

POTASSIUM

Occurrence.—Potassium salts are so essential to soil fertility that the location of workable deposits is of great importance. Feldspar is widely distributed and is responsible by its slow weathering for the available potassium salts in fertile soils. However, the amount removed by continued heavy cropping is not rapidly replaced from this source. As a result the whole civilized world paid tribute to Germany for its possession of the great Stassfurt deposits of the soluble chloride and sulfate of potassium. The Stassfurt mines began commercial production about 1861, just after Liebig showed the need of potassium in agriculture. The average depth of these mines varies from 1300 to 2000 feet.

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[1] *J. Am. Chem. Soc.*, *50*, 1625, (1928); *ibid.*, *51*, 3233, (1929); *Chemical Abstracts*, *21*, 1773, (1927).

With Alsace-Lorraine, France secured valuable deposits similar to those at Stassfurt. The minerals dug out at greatest profit are sylvite, KCl, and carnallite, $KCl \cdot MgCl_2 \cdot 6\ H_2O$. Other layers contain sulfates of potassium, magnesium and calcium with great quantities of sodium chloride. Many millions of tons of these salts have been removed and German authorities claim the deposit will last 1000 years.

A Russian potash deposit between Solikamsk and Borovaya, discovered in 1926, is estimated to contain 300,000,000 tons of K_2O.

The annual American demand for "potash" is about 300,000 tons (estimated as K_2O) most of which we import from Germany. However, if all our potash wastes (cement dust, blast-furnace dust, distillery slops, beet sugar water) as well as Searles Lake brine were utilized, we could produce over 200,000 tons of potash annually.

Searles "Lake" in the Mohave desert of California, is a bed of crystallized salts about twelve square miles in area, 60 to 70 feet deep, and saturated with brine. Depending on the season, this brine stands just above or below the surface of the salt block. The light salts of sodium, potassium, and boron, includes 35,000,000 tons of potassium chloride. Its profitable separation in a climate often reaching the trying temperature of 115° F. and in defiance of foreign competition has been a genuine triumph. Searles Lake is now producing over 50,000 tons annually making our own total about 60,000 tons. Germany and France together produce 1,600,000 tons.

Deep drillings (800–1760 feet) in western Texas and southeastern New Mexico have proved the existence of great beds of valuable potassium salts, somewhat similar to those at Stassfurt.

Enormous deposits of readily-decomposed leucite carrying ten per cent of potash (K_2O) are found in Wyoming, but competition from European potash prevents exploitation of this source. Leucites are also found in Italy, and Poland has a large deposit of potassium salts.

The Dead Sea may be exploited for its enormous reserves of valuable salts. It is estimated that it contains 1,300,000,000 tons of potash, 853,000,000 tons of bromine (combined), 22,000,000,000 tons of magnesium chloride and vast quantities of sodium chloride.

Wood ashes have always furnished a moderate amount of potassium carbonate (the "lye" of colonial days) and small deposits of potassium nitrate are known.

Preparation.—Sir Humphry Davy is usually given credit for being the first to make potassium. In 1807, the same year he made sodium, he electrolyzed moistened potassium hydroxide. Yet it seems more than probable that an American chemist, James Woodhouse of Philadelphia, made the element at about the same time and quite independently of any knowledge of Davy's discovery. Woodhouse died in 1809 and it is certain that some time before his death he made potassium by reduction of "potash" from wood ashes with carbon.

Potassium may be prepared by electrolysis of the melted hydroxide or chloride, a method applicable to all the alkali metals.

Properties.—Potassium is a silvery white metal, soft, easily tarnishing in air, and reacting violently with water. It is a more active element than sodium, but resembles it in uniting directly with hydrogen, oxygen, the halogens, nitrogen, and other elements. Its vapor is blue and its solution in liquefied ammonia is blue.

Potassium Chloride and Other Compounds.—The chloride is found nearly pure as sylvite in the Stassfurt deposits. Still more is obtained by cooling a hot, saturated solution of carnallite, $KCl \cdot MgCl_2 \cdot 6\,H_2O$. The less soluble potassium chloride crystallizes out.

The bromide is prepared by the action of bromine on a solution of potassium hydroxide. On heating, the bromate is converted into bromide:

$$6\,KOH + 3\,Br_2 \longrightarrow 3\,H_2O + 5\,KBr + KBrO_3.$$

Exercise 7.—Represent the above reaction by step equations.

Potassium Bromide is also made by adding potassium carbonate to the solution obtained by mixing bromine and iron. Compare with the methods of making sodium bromide. The *iodide* is prepared by methods similar to those used for sodium iodide. Both potassium bromide and iodide are used in photography and medicine.

Potassium Hydroxide.—Potassium hydroxide is very similar to sodium hydroxide in preparation, properties, and uses. Its chief use is in making soft and liquid soaps.

Potassium Carbonate.—Potassium carbonate is prepared by heating a mixture of magnesium carbonate and potassium chloride. Its chief use is in making hard glass.

Potassium Chlorate.—Potassium chlorate was discussed on page 191.

Potassium Cyanide.—Potassium cyanide is similar in every way to sodium cyanide.

Potassium Nitrate.—Potassium nitrate has long been used in gunpowder. It was formerly obtained in small deposits in Bengal, hence the name, Bengal saltpeter. Scheele discovered oxygen by heating this salt. It is now prepared by mixing saturated solutions of sodium nitrate and potassium chloride. On cooling, the less soluble potassium nitrate crystallizes out:

$$KCl + NaNO_3 \rightleftarrows NaCl + KNO_3.$$

It forms rhombic crystals melting at 345°. Some of it is used in medicine, some to preserve meat, which it colors red, but most of it is still used in black gunpowder. This explosive is essentially 75 parts potassium nitrate, 10 parts sulfur, 14 parts charcoal, and 1 part water. It is mixed and ground wet and then dried carefully. On explosion, expanding gases form. The smoke is due to solid potassium sulfide:

$$2\ KNO_3 + 3\ C + S \longrightarrow N_2 + 3\ CO_2 + K_2S.$$

Tests for Potassium Compounds.—The potassium flame is violet, but is easily masked by the intense yellow of the sodium flame. It is well to view the flame through a thick blue glass, which cuts off the yellow light.

The potassium ion unites with the chloroplatinate ion to form insoluble potassium chloroplatinate, K_2PtCl_6:

$$H_2PtCl_6 + 2\ KCl \longrightarrow 2\ HCl + K_2PtCl_6.$$

The precipitate is composed of yellow octahedra. The solution of potassium salt must be rather concentrated and precipitation is aided by addition of a little alcohol. This reaction is the basis of a standard method of determining potassium quantitatively. Due to the great expense of the chloroplatinic acid the perchlorate method is coming into use. Perchloric acid is added to a solution of a potassium salt. White potassium perchlorate, $KClO_4$, is precipitated, particularly in the presence of alcohol.

AMMONIUM

Ammonia gas, NH_3, has been discussed and we are familiar with the fact that it unites directly with hydrogen chloride to form a salt, ammonium chloride:

$$NH_3 + HCl \longrightarrow NH_4Cl.$$

The existence of this and other salts containing the ammonium radical, NH_4, makes it necessary to class this radical with the alkali metals. It is true the radical has never been isolated, but in its compounds it strongly resembles sodium and potassium.

The nearest we have come to isolating this "hypothetical metal" is in the preparation of *ammonium amalgam.* On electrolyzing a concentrated solution of an ammonium salt with a mercury cathode, the ammonium ion NH_4^+ is discharged on the mercury in which the metal dissolves or amalgamates. Mercury never dissolves anything but a metal. Addition of a dilute sodium amalgam to a cold concentrated solution of ammonium chloride also yields ammonium amalgam:

$$NH_4Cl + Na(Hg) \rightarrow NaCl + NH_4(Hg).$$

On allowing the solution to become warm the amalgam becomes astonishingly voluminous, due to the formation of ammonia and hydrogen. Finally only mercury and salt are left in the water. Evidently the ammonium displaces hydrogen from water just as sodium does:

$$2\ NH_4(Hg) + 2\ H_2O \rightarrow 2\ Hg + H_2 + 2\ NH_4OH,$$
$$NH_4OH \rightarrow NH_3 + H_2O.$$

Ammonium Hydroxide, NH_4OH.—This base is formed by union of ammonia gas with water:

$$NH_3 + H_2O \rightleftarrows NH_4OH.$$

It seems probable that in a 0.1 N solution, for example, most of the ammonia is merely in solution as NH_3 and only a little of it in the combined form of NH_4OH. Ammonium hydroxide is ranked as a weak base and it may be weak, but it is also possible that the small amount of actual ammonium hydroxide present may ionize very well. This base is used in washing. The oxide has never been prepared.

Ammonium Chloride, NH_4Cl.—This salt crystallizes in cubes or octahedra. At 350° it dissociates into ammonia and hydrogen chloride. On cooling the gases unite to form a smoke of ammonium chloride. The equilibrium is displaced by change in temperature:

$$NH_4Cl \rightleftarrows NH_3 + HCl.$$

If heated in an atmosphere of either ammonia or hydrogen chloride, the equilibrium would be displaced to the left. Better "opportunity for contact" between the two gases accounts for this. "Mass action" is another phrase for the same thing. The salt is made by passing ammonia into hydrochloric acid or by heating together ammonium sulfate and sodium chloride. Its use in soldering depends on its ability to clean off oxides, allowing metallic surfaces to be brought into contact. Its largest use is in the manufacture of over 500,000,000 dry cells each year in the United States alone.

Ammonium Sulfate, $(NH_4)_2SO_4$.—The sulfate is a product of coal gas works. Ammonia is passed directly into sulfuric acid, forming this salt. It is the source of many other ammonium compounds. As a source of nitrogen in fertilizers it is needed to the extent of half a million tons in this country alone. Germany uses nearly as much.

Ammonium Nitrate, NH_4NO_3.—There are three transition points of this salt, at 35°, 83°, and 126°. It melts at 160° and at higher temperatures decomposes into water and nitrous oxide:

$$NH_4NO_3 \longrightarrow 2\ H_2O + N_2O.$$

Most ammonium salts on heating yield ammonia, but this is an exception. It explodes if heated too rapidly (page 318).

Ammonium Nitrite, NH_4NO_2.—The unstable nitrite must be prepared as needed by mixing solutions of any ammonium salt with any nitrite. On gently warming the mixture nitrogen is evolved:

$$NaNO_2 + NH_4Cl \rightleftarrows NaCl + NH_4NO_2,$$
$$NH_4NO_2 \longrightarrow 2\ H_2O + N_2.$$

Ammonium Carbonate, $(NH_4)_2CO_3$.—Saturation of ammonium hydroxide with carbon dioxide produces ammonium bicarbonate, $(NH_4)HCO_3$. This decomposes easily on heating, yielding ammonia, carbon dioxide, and water, hence its use as a sort of baking powder. Addition of excess ammonium hydroxide to this salt forms normal carbonate which is rather unstable. The commercial product is a mixture of the bicarbonate and ammonium carbamate, $NH_4CO_2NH_2$. To prepare it powdered calcium carbonate is mixed with ammonium sulfate and sublimed.

Ammonium Sulfide, $(NH_4)_2S$.—Where ammonia and hydrogen sulfide gases are mixed in proper proportions the normal sulfide, $(NH_4)_2S$, or the acid sulfide, $(NH_4)HS$, may be formed. Saturation of a solution of ammonium hydroxide with hydrogen sulfide yields the soluble ammonium hydrosulfide. Addition of excess ammonium hydroxide to this solution yields the normal sulfide:

$$(1) \quad NH_4OH + H_2S \rightleftarrows (NH_4)HS + H_2O,$$
$$(2) \quad (NH_4)HS + NH_4OH \rightleftarrows H_2O + (NH_4)_2S.$$

The normal sulfide, which is colorless, is rather unstable because of hydrolysis, as indicated by the reversibility of reaction (2). It is much used in qualitative analysis to precipitate certain sulfides. Excess ammonium hydroxide helps to retard this hydrolysis. On standing, especially in the light, the air oxidizes the hydrogen sulfide released. The sulfur formed unites directly with the ammonium sulfide to form such yellow or red polysulfides as $(NH_4)_2S_2$, $(NH_4)_2S_3$, and $(NH_4)_2S_5$. This solution of "yellow" ammonium sulfide is used in analysis to dissolve the sulfides of arsenic, antimony, and tin.

Tests for Ammonium Salts.—These salts are isomorphous with potassium salts and form similar precipitates. However, they may be distinguished without great difficulty. All ammonium salts on warming with a base give off ammonia gas, recognized by odor and by its ability to turn moist red litmus paper blue:

$$(NH_4)_2SO_4 + Ca(OH)_2 \longrightarrow CaSO_4 + 2\ NH_4OH,$$
$$NH_4OH \rightleftarrows NH_3 + H_2O.$$

RUBIDIUM AND CÆSIUM

Bunsen and Kirchoff, in 1860, working with the spectroscope which they had just invented, discovered certain peculiar bright lines in the spectrum of the residue from a spring water. This clue led them to the discovery of the elements, rubidium and cæsium, responsible for the lines. Rubidium (*rubidius*, dark red) receives its name from two very bright red lines, and cæsium (*cæsius*, sky-blue) from two bright blue lines. Compounds of these elements are found in very small amounts in carnallite and in lepidolite. There is a small deposit of the mineral *pollucite* containing 34 per cent cæsium (estimated as the oxide).

The elements are of no great practical interest yet rubidium is now found to be the quickest acting metal for photoelectric cells used in television, etc. (p. 450). In a general way their chemistry is much like that of the rest of the alkalies. They are the most active elements of the group, taking fire at ordinary temperatures when exposed to dry oxygen.

EXERCISES

8. How many cubic centimeters of carbon dioxide (standard conditions) will be released by heating 72 g. of sodium bicarbonate?

9. Assuming 90 per cent recovery, what weight of baking soda will be obtained by the Solvay process from 200 Kg. of common salt?

10. How much sodium chloride would be necessary for the preparation of 1 ton of sodium hydroxide?

11. Extend this chart:

$$\begin{tikzcd}
NaCl \arrow[r] \arrow[d] & NaOH \arrow[r] & Na \arrow[r] & \text{etc.} \\
Cl_2 \arrow[d] & & & \\
HCl \arrow[r] & Cl_2 \arrow[r] & HClO \arrow[r] & \text{etc.}
\end{tikzcd}$$

CHAPTER XXXIX

THE ALKALINE EARTH METALS

Element	Atomic Weight	Density	Melting Point	Specific Heat
Calcium ....(Ca)	40.1	1.55	810°	0.152
Strontium ....(Sr)	87.63	2.54	900°	—
Barium ....(Ba)	137.37	3.75	850°	0.068

To this list should be added radium, but due to its peculiar relation to uranium it will be discussed in connection with that element. The metals of this group are like the alkalies in that they form rather strong bases. A fancied resemblance to the "earthy" (earth-like) oxides of iron and aluminum led to the old name, "alkaline earths."

All the elements are divalent in their compounds. All are active, displacing hydrogen from cold water with moderate speed. They are silvery white metals when freshly cut, but quickly tarnish in air due to formation of the oxides and probably the carbonates. They are somewhat harder than lead.

All are made by electrolysis of their melted chlorides or hydroxides, but none have, as yet, any commercial use. Calcium hydroxide is slightly soluble (lime water) and strontium hydroxide and barium hydroxide somewhat more so. The sulfate of barium is extremely insoluble (1 : 400,000), of strontium rather insoluble (1 : 8000), while calcium sulfate is slightly soluble (1 : 500). All the carbonates are insoluble, while the bicarbonates are soluble.

CALCIUM

Occurrence.—Calcium compounds are very common in the earth's crust. The most important is the carbonate, $CaCO_3$. Gypsum, $CaSO_4 \cdot 2\ H_2O$, is very plentiful. The best of the few great deposits of the fossil rock, phosphorite, $Ca_3(PO_4)_2$, are in the United States and North Africa. Other calcium minerals are apatite, $3\ Ca_3(PO_4)_2 \cdot CaF_2$ or $3\ Ca_3(PO_4)_2 \cdot CaCl_2$, fluorspar, CaF_2, and dolomite, which is a mixture of the carbonates of calcium and magnesium. The solid matter of bones is largely calcium phosphate, making the calcium content of the entire body 1.5 per cent.

Preparation.—In 1808 Davy prepared the three alkaline earth metals by electrolysis of their fused hydroxides. Calcium is now made by electrolysis of the melted chloride in a carbon or iron cell. The metal is molten when liberated and floats to the top of the bath, where it is chilled and slowly lifted out as a growing stick. In one process this solid stick of calcium forms the cathode.

Properties.—Calcium is a silver-white metal, melting at 800°. Its density is 1.55. The metal can be rolled and drawn. When hot it can be worked much more easily, but oxidation increases rapidly with rise in temperature. The hot metal unites readily with both oxygen and nitrogen; hence it can be used in securing a vacuum. Its nitride yields ammonia in contact with water:

$$Ca_3N_2 + 6\ H_2O \longrightarrow 3\ Ca(OH)_2 + 2\ NH_3.$$

With hydrogen the hot metal forms a solid hydride known commercially as ***hydrolite.*** This is a convenient, portable source of hydrogen for military purposes:

$$CaH_2 + 2\ H_2O \longrightarrow Ca(OH)_2 + 2\ H_2.$$

Calcium Carbonate.—Vast beds of limestone are found in most countries. Other forms of the carbonate are marble (composed of small calcite crystals) and chalk. Marl is a mixture of limestone and clay. Chalk is made up of the skeletons of minute marine organisms. Sea-shells, corals, pearls, and egg shell are familiar forms of calcium carbonate.

Pure crystallized calcium carbonate is found in two forms, aragonite and calcite, differing in crystal shape and density. When the carbonate is formed in solutions above 30° aragonite crystals deposit, but below 30° calcite crystals are obtained.

Calcium carbonate is practically insoluble in water, as one liter holds only 13 mg. of the salt. But when water is saturated with carbon dioxide the solubility of the carbonate increases thirty fold. To be exact, the bicarbonate is formed:

$$CaCO_3 + H_2CO_3 \longrightarrow Ca(HCO_3)_2.$$

Rain washes the carbon dioxide of the air into the soil and as this carbonated water trickles over beds of limestone the soluble bicarbonate forms and the rain water becomes "hard." In many places underground caves are formed in this manner. Some springs deposit this dissolved rock when the sudden decrease of pressure on the water allows the escape of carbon dioxide. Travertine, the rock used in building ancient Rome, was formed in this way. Marble is familiar as an ornamental building material.

Limestone has many uses. As a source of lime it is mined in great quantities. Cement, glass, and ceramic material require much more. Modern agriculture approves the use of ground limestone as well as lime in correcting the acidity of soils. Calcium carbide and cyanamide both require limestone or lime as a raw material.

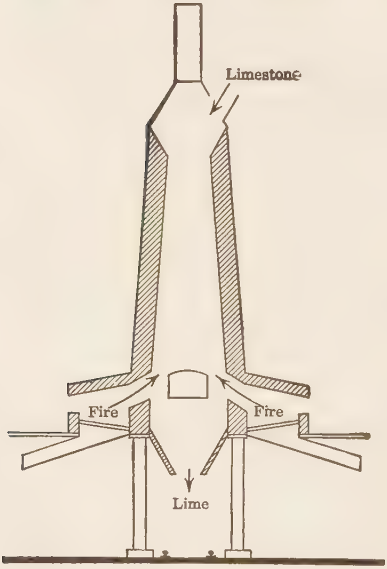

FIG. 141.—A lime kiln.

Calcium Oxide, CaO.—This oxide, known as quicklime, is usually obtained by heating limestone:

$$CaCO_3 \rightleftarrows CaO + CO_2.$$

At ordinary temperatures the vapor tension of carbon dioxide from limestone or any similar carbonate is too small to measure. But at elevated temperatures this pressure becomes more than appreciable. As a rule lime kilns operate at temperatures of 750°–900°. Of course if the lime were allowed to cool in an atmosphere of carbon dioxide the carbonate would be formed again, since it is a reversible reaction, but this is not done.

The vapor pressures of carbon dioxide from calcium carbonate at various temperatures show why a lime kiln is operated at a bright red heat.

587°	701°	748°	840°	894°	898°
1 mm.	23 mm.	70 mm.	311 mm.	716 mm.	760 mm.

The modern kiln is heated by indirect firing (Fig. 141). Two furnaces are built against the sides of the tower and the flames from wood, coal, or oil are led into the tower without introduction of ash. Wood is better than coal because the flame is longer. Also the moisture in the wood helps to sweep out the carbon dioxide, thus aiding decomposition of the carbonate. Sometimes a jet of steam is introduced for the same purpose. But wood is now practically unattainable. The gas-fired kiln is best and to-day there are groups of six towers arranged around one gas producer. Some towers are 60 feet high and 7 feet wide, inside. Such kilns are continuous in operation, producing over 25 tons of lime daily for each tower. With producer gas as the fuel one ton of coal burns 5 or 6 tons of lime. Still wider kilns producing 60 tons daily have been built. Rotary kilns are also in use.

If the temperature exceeds 1200°, the surface of some lumps fuses, due to impurities. When such lime is used on finished surfaces, these lumps may be slow to slake. Later they expand and cause blistering.

Calcium oxide is a white solid melting at about 2750° and boiling at higher temperatures. Heated by the oxyhydrogen flame it becomes brilliantly incandescent and was once used as a source of light for lantern projection (the "lime light"). In the electric arc the oxide vaporizes. On condensing, these vapors form crystals. Calcium oxide is very difficult to reduce. Potassium and sodium are able to reduce it only at the temperature of the electric furnace.

Pure calcium oxide takes up 31.1 per cent of its own weight of water, but the usual impurities lessen this amount. As the oxide hydrates to form the hydroxides much heat is evolved. In fact quicklime stored in wood has often caused fires by accidental reaction with water. Considerable increase in volume also takes place on slaking. The water is first adsorbed and then reacts:

$$CaO + H_2O \longrightarrow Ca(OH)_2.$$

On long exposure to the air quicklime becomes "air slaked," changing into the hydroxide and the carbonate.

The United States uses five millions of tons of lime for water softening, sugar clarifying, and the manufacture of mortar, plaster, bleaching powder, sprays, paper, leather, and sand-lime bricks. Some gases are dried over lime. Some uses named for limestone apply to quicklime. In agriculture, soil acidity is neutralized by either lime or limestone. However, too much quicklime causes an actual loss of soil nitrogen in the form of ammonia to the air. Ground limestone can do no harm.

Calcium Hydroxide, $Ca(OH)_2$.—Slaked lime is a white powder formed by careful addition of water to quicklime. It is slightly soluble, 100 cc. of water dissolving 0.17 g. at 18°. At higher temperatures it is less soluble. The little that is in solution ionizes rather well, but when considerable quantities of a base are required it is customary to use a suspension of the solid in water known as "milk of lime." As fast as the little in solution is used up some of the suspended hydroxide goes into solution:

$$\underset{\text{Undissolved}}{Ca(OH)_2} \rightleftarrows \underset{\text{Dissolved}}{Ca(OH)_2} \rightleftarrows \underbrace{Ca^{++} + OH^- + OH^-}_{\text{Ionized}}.$$

This is the cheapest base known and has many industrial uses. In making mortar, plaster, alkalies, bleaching powder, purifying illuminating gas, removing hair from hides, and clarifying sugar solutions it is important. Naturally some of these uses duplicate those for the oxide.

Mortar.—Mortar, to the bricklayer, is a mixture of slaked lime, sand, and water which hardens slowly by drying. The chemist knows that carbon dioxide of the air penetrates the wet mortar and reacts with the calcium hydroxide to form solid interlacing crystals of calcium carbonate, $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$. The sand, preferably with sharp edges, merely gives bulk, rigidity, increases porosity, and reduces shrinkage. Yet even the chemist is surprised to learn that some mortar in Roman walls 2000 years old has not been completely carbonated. Evidently mere drying does not account for much of the solidity of mortar. Possibly the colloidal particles of calcium hydroxide "set" in some way suggestive of the drying of glue or water glass. Wall plaster differs from mortar only in containing hair as a binder. It is porous enough to allow considerable circulation of air through the walls.

Calcium Sulfate, $CaSO_4$.—The dihydrate of this salt, $CaSO_4 \cdot 2\ H_2O$, is found as gypsum in Michigan, Ohio, New York, Virginia, Kansas, Oklahoma, and other states and is mined to the extent of 6,000,000 tons annually. It is heated just enough to cause the loss of three-fourths of its water, leaving the hemihydrate, $2\ CaSO_4 \cdot H_2O$, or plaster of Paris. This residue, when mixed with the proper amount of water, sets to a white solid in from 5 to 15 minutes. What really happens is a reaction producing interlacing crystals of the dihydrate. The white finishing coat of common plastered walls contains plaster of Paris. Statuary is often made from it, because the material expands slightly on setting, thus taking a very sharp impression of the mold. For commercial work, such as white plaster, stucco, and interior wall bricks, and wallboard, the setting process is retarded by glue or a product made by digesting hair with sodium hydroxide. The anhydrous salt is used in making Keene cement, as a hard-finish plaster, and as a filler for glazed paper. The United States uses over 2,000,000 tons of gyspum annually, most of it for plaster.

Calcium Chloride, $CaCl_2$.—The mineral tachydrite, $CaCl_2 \cdot MgCl_2 \cdot 12\ H_2O$, occurs in the Stassfurt salt layers. Some calcium chloride is found in salt brines and is removed from the bitter liquors. Most of the supply, however, is obtained as a by-product in the ammonia soda process. The hexahydrate, $CaCl_2 \cdot 6\ H_2O$, crystallizes from very concentrated solutions at ordinary temperatures.

As a drying agent calcium chloride has its limitations. Ammonia cannot be dried over it because of the formation of $CaCl_2 \cdot 8\ NH_3$. For a similar reason it is not suitable for the dehydration of alcohol. Concentrated sulfuric acid is a better dryer and phosphorus pentoxide the most powerful of all. Even $CaCl_2 \cdot H_2O$ has an appreciable vapor tension and so its action is a trifle short of perfect drying. More of this salt is produced commercially than is needed. It finds a limited market as a dust layer, in anti-freeze solutions, in coal washing, in tempering metals, and chiefly in forming a refrigerating brine for ice plants and cold storage buildings.

Calcium Fluoride, CaF_2.—This salt occurs in nature as the mineral fluorspar. It melts at 1330° and is in demand as a slag former in metallurgy. Addition of calcium fluoride to some other salts lowers the melting point of the mixture. Opaque glass and enamels are often made with addition of fluorspar. As a source of hydrofluoric acid it is already familiar to the student.

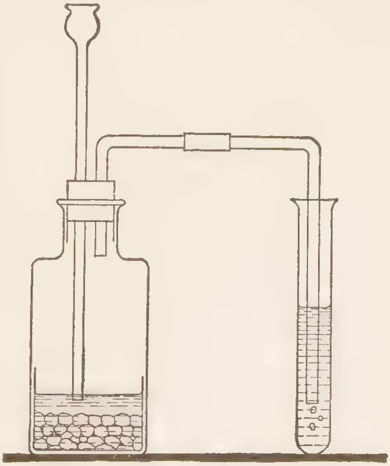

Fig. 142.—Passing carbon dioxide into lime water.

Hardness of Water.[1]—Natural waters in contact with deposits of limestone or dolomite dissolve appreciable amounts of these rocks if carbon dioxide is present, as it always is. The soluble bicarbonates of calcium and magnesium formed give ***temporary hardness*** to the water, temporary because, on heating, these bicarbonates decompose with precipitation of the normal carbonates. In the case of magnesium it is the less soluble basic carbonate that precipitates.

Pass carbon dioxide into clear lime water (Fig. 142). A precipitate of the carbonate forms. An excess of carbon dioxide dissolves this precipitate—the water has acquired temporary hardness. Now boil the solution and note the formation of insoluble calcium carbonate, not by evaporation but merely by raising the temperature.

$$\begin{aligned} &(1)\quad Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O, \\ &(2)\quad CaCO_3 + H_2CO_3 \longrightarrow Ca(HCO_3)_2, \\ &(3)\quad Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2. \end{aligned}$$

Permanent hardness is due largely to calcium and magnesium sulfates, which are not precipitated by mere boiling, unless the solution is made very concentrated by evaporation. A comparison of solubilities at ordinary temperatures is interesting.

Permanent hardness	1 liter of water dissolves	0.013 g. $CaCO_3$
	1 liter of water dissolves	1.000 g. $MgCO_3$
	1 liter of water dissolves	2.000 g. $CaSO_4$
	1 liter of water dissolves	354.000 g. $MgSO_4$

As a matter of fact, no natural water contains enough magnesium bicarbonate to cause precipitation of magnesium carbonate (solubility, 1 gram per liter) on boiling without evaporation. In certain districts some of the temporary hardness is due to ferrous bicarbonate, $Fe(HCO_3)_2$.

Hardness in commercial practice in this country is measured in grains per gallon or in parts per million, "p.p.m.," of calcium carbonate. That is, one degree of hardness (United States) is 1 grain per gallon (0.017 gram per liter) or 17 p.p.m.

Softening Water.—The importance of softening water is great. In boilers a hard scale of salts is left by the evaporation of feed water. This scale is a poor conductor of heat and causes a serious waste of fuel. A layer of one-eighth inch thick causes a loss of 10–12 per cent of fuel. This loss increases as the square of the thickness. Furthermore superheating of the boiler may result. Cracking of the brittle scale may admit water to the overheated iron, causing an explosive generation of steam. If the temperature of the iron rises too high, a layer of the oxide, Fe_3O_4, forms, weakening the boiler to the danger point.

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[1] In Cady's *Inorganic Chemistry*, page 425, is given a good discussion of methods of determining the proper amounts of softeners to add to hard water.

Hardness of water causes an appalling waste of soap. No lather can form and consequently no cleansing be achieved until all the hardness has been precipitated at the expense of the soap. Thus, with sodium oleate, representing a typical soap, we have:

$$2\ \mathrm{Na}\cdot\mathrm{Oleate} + CaSO_4 \longrightarrow Na_2SO_4 + \mathrm{Ca}\cdot\mathrm{Oleate}.$$

A further annoyance is caused by the stickiness of the calcium oleate formed. All calcium soaps are insoluble and curdy.

There is a loss of wastage of one-fifth of a pound of soap per 1000 gallons for every part per million of hardness. For water of 300 p.p.m. hardness and soap at 5 cents per pound this waste would cost a city of 40,000 people fully $100.00 daily.

One of the cheapest softeners is lime itself. This sounds to the public like making matters worse, for it is often said that "lime causes the hardness of water." However, the following equations show the explanation of the paradox:

$$(1)\quad Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2\ H_2O + 2\ CaCO_3 \downarrow,$$
$$(2)\quad Fe(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2\ H_2O + CaCO_3 \downarrow + FeCO_3 \downarrow,$$
$$(3)\quad MgCO_3 + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + Mg(OH)_2 \downarrow.$$

Reaction (3) is worthy of special attention. Either the bicarbonate or normal carbonate of magnesium is converted by any base into the decidedly insoluble hydroxide. Remember that one liter of water dissolves 1 g. of $MgCO_3$ but only 0.01 g. of $Mg(OH)_2$. To precipitate permanent hardness crude "soda ash" is used:

$$CaSO_4 + Na_2CO_3 \longrightarrow Na_2SO_4 + CaCO_3 \downarrow.$$

Sodium hydroxide is not as cheap, but it takes care of both kinds of hardness because the sodium carbonate produced in the following reaction reacts with the permanent hardness as indicated above:

$$Ca(HCO_3)_2 + 2\ NaOH \longrightarrow 2\ H_2O + CaCO_3 \downarrow + Na_2CO_3.$$

The common practice to-day is to use both lime and soda ash, varying the proportions with the seasonal variations in the water content. The limit of lime-soda softening is 50 p.p.m., which represents the combined solubilities of $CaCO_3$ and $Mg(OH)_2$. Trisodium phosphate is used somewhat as a softener. It is powerfully alkaline by hydrolysis and in addition causes formation of insoluble phosphates.

Cities with supplies of hard water may do well to consider the merits of a municipal softening plant. One pound of cheap lime softens as much water as 20 pounds of soap.

Boiler compounds usually consist of soda ash or sodium phosphate with tannic acid, starch, or some gummy material (protective colloid) that prevents the formation of a hard, compact scale. Graphite or talc are added by some engineers for the same purpose, but their use is questionable. A loose scale can be blown out at intervals. Boiler compounds are introduced in the boiler, but it is much better to soften the water outside the boiler in settling tanks.

The very modern ***permutit process*** (Fig. 143) of softening yields water of zero degrees of hardness. No other chemical will do this in practice. An artificial zeolite (really a sodium silico-aluminate) is prepared and dried so as to retain its porous structure. When hard water slowly flows through a bed of this Na·Permutit there is an exhange of calcium and magnesium for sodium.

$$Ca(HCO_3)_2 + 2\ Na\cdot Permutit \rightarrow 2\ NaHCO_3 + Ca(Permutit)_2.$$

After a time the permutit no longer functions, having become Ca·Permutit. Salt water (10 per cent) is then left on it for about 12 hours and, because the sodium chloride is now in excess, the Na·Permutit is regenerated. After washing out the salt it is ready for use again:

$$Ca(Permutit)_2 + 2\ NaCl \rightarrow CaCl_2 + 2\ Na\cdot Permutit.$$

Of course there is absurdity in the use of "Permutit" as a negative radical but it has convenience.

This reaction is really reversible, depending only on whether the sodium chloride or a soluble calcium salt is in excess. The value of the perfectly soft water produced by the permutit process is so great to the dye industry, the textile industry, and hotel or household water systems, that, in spite of its extra cost, installations are very numerous. The active material can be used and regenerated twenty years or longer.

There are many varieties of natural and artificial zeolites similar to permutit on the market. The molecular composition of a typical one is $Na_2O \cdot Al_2O_3 \cdot 5\ SiO_2$.

In the laundry it is best to soften the water with soda, borax, or trisodium phosphate *before* adding any soap. The sticky curds of calcium soaps, for example, soil the clothes and are hard to remove. Preliminary softening prevents this. Iron soaps, if not removed, would finally cause rusting spots. The cleansing action of soap was discussed in the chapter on Colloid Chemistry under Adsorption.

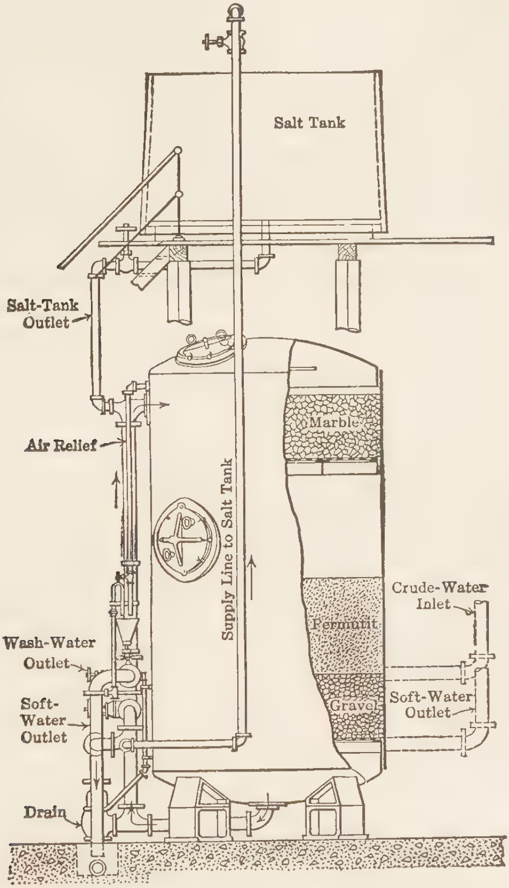
Salt Tank
Salt-Tank Outlet
Marble
Air Relief
Supply Line to Salt Tank
Crude-Water Inlet
Permutit
Wash-Water Outlet
Soft-Water Outlet
Gravel
Soft-Water Outlet
Drain

FIG. 143.—Permutit water softener.

Tests for Calcium Compounds.—The calcium flame is brick-red, but the extreme insolubility of white calcium oxalate is usually taken as the best test.

Barium

Occurrence.—The chief barium mineral is barite, $BaSO_4$. The United States produces 200,000 tons of this rock annually. Witherite, $BaCO_3$, is not so common.

Barium Sulfate, $BaSO_4$.—This mineral is the starting point for the preparation of all barium compounds, including the precipitated form of barium sulfate. Coal mixed with four times its weight of barite is roasted four hours in a rotating furnace. The barium sulfide formed is treated with water. It is not very soluble, but is slowly hydrolyzed to the more soluble hydrosulfide. By reaction with "salt cake," Na_2SO_4, the finely divided "blanc fixe" or precipitated barium sulfate is formed:

$$BaS + Na_2SO_4 \longrightarrow Na_2S + BaSO_4.$$

The sodium sulfide is a by-product necessary in making and using sulfur dyes. Blanc fixe is used, when pure white, as the body of lithograph inks and lake colors, and as filler for paints, rubber, linoleum, oilcloth, and glazed paper.

Other barium salts may be made by reaction of the sulfide with the proper compounds.

The Barium Oxides.—The monoxide is sometimes made by heating the nitrate:

$$2\,Ba(NO_3)_2 \rightleftarrows 2\,BaO + 4\,NO_2 + O_2.$$

It is also prepared by roasting the carbonate. However, barium carbonate is much more stable than calcium carbonate and must be heated above 1350° to secure rapid dissociation. The corresponding temperature for calcium carbonate is 898°. By heating barium carbonate with carbon the carbon dioxide is constantly removed by reduction to carbon monoxide. This lowers the partial pressure of the dioxide and thus facilitates decomposition of the carbonate:

$$BaCO_3 \rightleftarrows BaO + CO_2,$$
$$CO_2 + C \longrightarrow 2\,CO.$$

Barium monoxide is an excellent dryer for gases if prepared by heating barium carbonate mixed with coke to moderately high temperatures. The fused product is not so good. Barium oxide was once of interest in connection with the Brin process of making oxygen. It is now important mainly in preparing the dioxide by heating in air above 500°:

$$2\ BaO + O_2 \rightleftarrows 2\ BaO_2.$$

Barium peroxide is important now as a source of hydrogen peroxide. Almost any acid can be used in reaction with the barium compound, but in practice carbonic, sulfuric, and phosphoric are found most suitable. Since soluble barium salts are poisonous, hydrochloric acid will not do, as it would leave barium chloride in solution.

$$BaO_2 + H_2SO_4 \longrightarrow H_2O_2 + BaSO_4\downarrow.$$

Barium Hydroxide, $Ba(OH)_2$.—The hydroxide of barium is much more soluble than either calcium or strontium hydroxide. It is a moderately strong base and is used in quantitative analysis to absorb carbon dioxide.

Other Barium Compounds.—The nitrate, $Ba(NO_3)_2$, is used in green pyrotechnic signals and in some explosives. Its chief use is in manufacture of the oxides. The chloride, $BaCl_2$, has some use as a mordant for dyes and as a water softener. The chlorate is mixed with sulfur and charcoal to produce green fire. Barium carbonate with lime has been used in water softening.

Tests for Barium Compounds.—The barium flame is green (distinctive except for copper and boric acid). The usual tests involve the precipitation of yellow barium chromate and white barium sulfate, insoluble in dilute acids.

STRONTIUM

Occurrence.—The chief ores of strontium, like those of calcium and barium, are the carbonate, $SrCO_3$, and sulfate, $SrSO_4$. The sulfate, celestite, occurs in beautifully crystallized masses in a cave near Put-in-Bay and at other points along Lake Erie. The carbonate, strontianite, is not so plentiful. However, the little strontium ore we need is imported.

Strontium Nitrate, $Sr(NO_3)_2$.—This salt is mixed with sulfur, charcoal, and potassium chlorate to make red lights for signals or fireworks. Like most strontium compounds it is made by reduction of the sulfate with hot carbon and treatment of the strontium sulfide formed with the appropriate acid or salt.

Strontium Hydroxide, $Sr(OH)_2$.—The base is by far the most important strontium compound. It may be produced by heating the carbonate in a current of superheated steam:

$$SrCO_3 + H_2O \longrightarrow CO_2 + Sr(OH)_2.$$

In Europe large quantities are used in purifying beet sugar. To the sugar molasses heated above 100°, strontium hydroxide is added. This reacts with the sugar, forming crystals of strontium disucrate. These are filtered off, washed, and dissolved in a cold solution of strontium hydroxide. After standing several days half of the strontium hydroxide crystallizes out. Carbon dioxide is then passed into the solution. Strontium carbonate is precipitated, leaving the sugar in solution, free from all impurities. On evaporation in the vacuum pans a good grade of sugar is secured, needing no further refining.

Tests for Strontium Compounds.—The characteristic carmine red flame is an indicator of strontium. Precipitation of its carbonate, sulfate, and oxalate, all white salts, aids in testing for the element.

EXERCISES

1. What are the uses of barium sulfate?
2. How does soap soften water? How do lime and soda soften water?
3. What happens to quicklime piled in the open air?
4. From what industry is calcium chloride a by-product?
5. If you had 500 Kg. of barium sulfate how many Kg. of barium peroxide could you make, assuming complete conversion? How proceed?
6. A sample of hard water is found to contain 55 parts per million of calcium bicarbonate. How much lime would be required to soften ten million liters of this water? Ignore other sources of hardness.
7. A sample of water contains 70 parts per million of magnesium bicarbonate. How much lime would be required to soften 10 million liters of this water?
8. Calculate the atomic weight of calcium if 62.2152 g. of $CaCO_3$ give 34.9905 g. CaO on heating.
9. At 20° calcium hydroxide dissolves to the extent of 16.5 g. per liter (*a*) What is the solubility in gram-molecules per liter? (*b*) If the base is completely ionized what will be the concentration of each ion in terms of gram-ions per liter?

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CHAPTER XL

COPPER, SILVER, AND GOLD

The Group.—A glance at the periodic table reminds the student that Group I is made up of two families of metals. Placed on the left of the column are the alkali metals, while copper, silver, and gold are placed on the right. The most striking resemblance between the two sub-groups is in their common valence of one. Yet copper and gold have two valences. The alkali metals are strongly basic while copper and gold are weakly basic. Silver hydroxide is a strong base, but it is only slightly soluble.

The alkali metals are very soft, very light, melt at rather low temperatures, and are extremely active chemically. In these respects the other sub-group is distinctly different. Copper, silver, and gold are much harder, far heavier, and all three melt near 1000°. They are so inactive they do not react with water and, in fact, do not displace hydrogen from acids. Copper forms a very thin film of oxide in air, but gold and silver are not affected by air. This inactivity explains the occurrence of these three metals free in nature. Consequently they were known in ancient times. Their beauty made them especially desirable.

COPPER

Occurrence.—The world normally produces about 1,500,000 metric tons[1] of copper per year and of this total the United States furnishes one-half. Chile, Mexico, Africa, Japan, Canada, and Spain supply the rest. A large deposit of free copper occurs in Michigan around Lake Superior, but the chief ores are chalcocite, Cu_2S, and copper pyrites, $CuFeS_2$, found in Montana and Utah. Malachite, $Cu_2(OH)_2CO_3$, occurs in Arizona. California, New Mexico, Tennessee, and Alaska also possess great deposits of rich copper ores. We recover a few hundred thousand tons of copper each year from scrap.

Metallurgy.—The separation of native copper from the surrounding rock is largely mechanical. After grinding and washing, the ore is melted with a flux (to lower the melting point of the waste rock). The heavier melted copper is easily separated. The ease of extraction of copper from such ores made copper one of the first metals known to man. It was probably in use about 4000 B.C.

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[1] A metric ton is 1000 Kg. or about 10 per cent more than our common short ton.

Sulfide ores require a different treatment. They usually contain more or less iron. In general such ores are roasted to burn out the sulfur. The iron oxide resulting reacts with added sand to form the fusible slag, ferrous silicate. For detailed modern methods we can do no better than consider the process used near Butte, Montana. Here in an area of three or four square miles one-tenth of all the copper produced by the world is mined, 5,000,000 tons to date. It is smelted a few miles away at Anaconda.

Obviously, ores containing 3 per cent copper must be ***concentrated*** before smelting, and this is done by a series of grinding, washing and flotation operations (p. 469). The product, carrying 8 per cent copper, is next ***roasted*** to remove 80 per cent of the sulfur. Some sulfide is necessary to permit the formation of "matte." After a roasting furnace is started no more fuel is needed because the heat of the burning sulfur is sufficient. The charge is brought to a red heat, but not allowed to melt.

After roasting, the hot charge is ***smelted*** in enormous ***reverberatory furnaces,*** usually about 27 feet wide and 144 feet long. These furnaces are lined with silica brick and have arched roofs to radiate heat down on the charge. The floor, however, is of magnesite. They are fired with powdered coal blown in by a jet of compressed air. Some silica and alumina are left in the charge from the original ore, but limestone is added to aid in the formation of a fusible slag. Much iron is removed in the slag. A heavy molten mixture of sulfides of copper and iron called ***" matte "*** is removed and taken to the ***converters,*** where a blast of air burns out the remaining sulfur and oxidizes the iron and other impurities. A converter is made of a shell of heavy steel plate lined with magnesite brick. The inside dimensions are usually 16 feet diameter and 15 feet depth although the Anaconda converters are 20 feet wide. At the back and near the bottom a line of tuyère pipes admit compressed air at 16 lbs. The iron oxide formed combines with silica and alumina of some raw ore added for this purpose to form slag, which is poured off by tilting the converter. The 65-ton charge of matte is blown about 5 hours, while the Bessemer converter used in steel making is blown only 15 minutes. The converter reactions are represented by the following equations:

$$2\ FeS + 3\ O_2 \longrightarrow 2\ FeO + 2\ SO_2 + 221{,}920\ cal.,$$
$$FeO + SiO_2 \longrightarrow FeSiO_3,$$
$$2\ Cu_2S + 3\ O_2 \longrightarrow 2\ Cu_2O + 2\ SO_2,$$
$$Cu_2S + 2\ Cu_2O \longrightarrow 4\ Cu + SO_2.$$

After converting, the last traces of iron, sulfur, and slag are removed in a refining furnace (much like the reverberatory) and heated with powdered coal also. Air is blown through the liquid metal oxidizing the last of the iron and sulfur and a little copper. To reduce the copper oxide, the liquid is stirred by green wooden poles. Reducing gases escape.

The converter product, 99 per cent blister copper, is then cast into heavy plates for electrolytic refining.

Electrolytic Refining.—Since the leading use of copper (as a conductor of electricity) demands a metal 99.95 per cent pure, it is necessary to remove all but traces of the arsenic, lead, silver, gold and zinc impurities. As little as 0.03 of 1 per cent arsenic lowers the conductivity of copper about 14 per cent. The slabs of cast copper from the smelters are made anodes in a bath of copper sulfate acidified with sulfuric acid. The cathodes are very thin sheets of pure copper arranged alternately with, and very close to, the anodes. The Cu^{++} ions are attracted to the cathode, where they are discharged and deposited. An equal number of Cu^{++} ions are formed by the metal of the anode, passing into solution. The gold and silver have less tendency to ionize, so they drop to the bottom of the huge vat as a mud mixed with other impurities. Any zinc present in the anode would ionize more readily than the copper and would deposit on the cathode if the Cu^{++} ions were not so much more easily discharged. Very little difference of potential is needed, less than 0.5 volt. As measured in quantity of electricity Faraday's law shows that one equivalent weight of copper is deposited for every 96,500 coulombs of electricity. The value of the gold and silver recovered from the sludge is astonishing. In fact 80 per cent of the silver production and 15 per cent of the gold production of the world are recovered as by-products in the refining of copper, lead, nickel, and cobalt.

One great copper refinery in the United States in the electrolytic purification of 264,000 tons of copper recovered (in a single year):

19,000,000 ounces of silver
233,000 " " gold
1,000 " " palladium
500 " " platinum

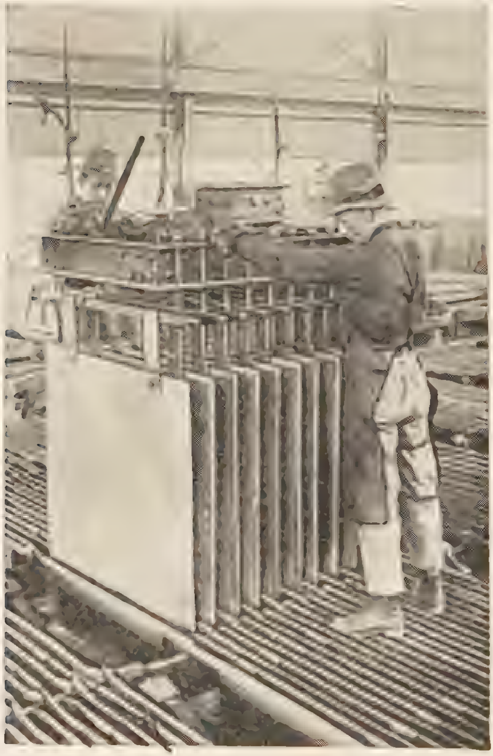

FIG. 144.—Purifying copper by electrolysis.

Leaching Copper Sulfide Ores.—Chalcopyrite ore, $CuFeS_2$, is often leached in large ventilated piles. wet with a spray or trickle of water and exposed to the air. The temperature sometimes reaches 80°–90° C. and must not fall below 40° C. if the action is to continue. After a few years the action is completed. In the filtered liquors is soluble copper sulfate.

$$Cu_2Fe_2S_4 + 2\,Fe_2(SO_4)_3 + H_2O + 7\,O_2 \rightarrow 6\,FeSO_4 + 2\,CuSO_4 + 2\,H_2SO_4.$$

If the ore is simply Cu_2S without iron the action is

$$Cu_2S + 2\,Fe_2(SO_4)_3 + H_2O + 3\,O \rightarrow 4\,FeSO_4 + 2\,CuSO_4 + H_2SO_4.$$

On throwing scrap iron into the liquors the less active metallic copper is precipitated by the more active iron.

$$CuSO_4 + Fe \rightarrow FeSO_4 + Cu.$$

About 1.5 to 2.0 pounds of iron are required to precipitate one pound of copper because some iron is consumed in reaction with the acid and the ferric sulfate.

Properties of Copper.—Copper is red by reflected light, but greenish by transmitted light. The two colors may be observed with thin sheets such as "Dutch foil." It melts at 1083° and boils at about 2300°. The melting point in air is lowered about 20° by the oxide formed, which is soluble in copper. The metal has a density of 8.93. It is remarkably malleable and ductile, and is the best electric conductor of the cheaper metals. If it lacked either in ductility or conductivity, there would not be much copper wire on the market.

A single crystal of copper (6 in. x 7/8 in.) has been made by W. P. Davey by the heating and very gradual cooling of copper in an electric furnace. Ordinary cooling of molten metals produces small crystals. The point of great interest here is the superior electrical conductivity of the single crystal, 14 per cent greater than for ordinary pure copper. It is probably the regular arrangement of the atoms in columns along the main axis that gives this increased conductivity as compared with ordinary copper, in which the crystals are small and placed in chaotic fashion. "A crystal the size of a lead pencil, given a sudden jerk with the finger, bent like soft wax, but once bent it acquired the properties of ordinary copper for the bending had transformed the large crystal into a mass of smaller ones." The commercial possibilities are attractive but problematical.

Although pure copper can not be tempered, hardened by heat treatment like steel, some new alloys containing approximately 96 per cent Cu, 1 per cent Mn and 3 per cent Si, show the physical properties of steel. They can be worked soft and then hardened by heat treatment.

Chemically, copper is rather inactive. It is not oxidized in dilute solution. In other words the cuprous ion is colorless while the cupric ion is blue. At high temperatures cuprous compounds are more stable than cupric compounds. All copper salts are poisonous, yet small amounts were once used to "green" canned peas, pickles, and other vegetables. Copper salts are especially poisonous to lower forms of life. For this reason carefully adjusted doses are sometimes added to water reservoirs to kill weed growth. All insoluble copper compounds except the extremely insoluble cupric sulfide are dissolved by alkali cyanides and by ammonium hydroxide.

The green coating acquired by copper roofing and bronze statues outdoors was once thought to be the basic carbonate. In cities it is the basic sulfate due to SO_3 in the air. On the sea it is the basic chloride.

Cuprous Oxide, Cu_2O.—This red oxide is found in nature as the mineral cuprite or ruby copper. In the laboratory it may be prepared by oxidizing copper at a gentle heat or by the addition of sodium hydroxide to a solution of cuprous chloride. Cuprous hydroxide is unknown, but it may possibly exist for an instant before losing water. The simplest way to prepare this oxide is to reduce ***Fehling's solution*** with glucose. This famous solution is a mixture of copper sulfate, sodium hydroxide, and Rochelle salts (or any tartrate). A complex copper tartrate ion is formed which yields so few simple copper ions that no cupric hydroxide is precipitated. Yet enough cupric hydroxide is in solution to be reduced to the very insoluble cuprous oxide by added glucose. Since the occurrence of glucose in the urine is a symptom of diabetes, the use of Fehling's solution in diagnosis must be important.

Cuprous Chloride, CuCl.—This white, sparingly soluble salt is made only by reduction of cupric chloride. Boiling copper with cupric chloride in a solution of hydrochloric acid (absence of air prevents oxidation) is adequate to insure reduction:

$$CuCl_2 + Cu \longrightarrow 2\ CuCl.$$

Cupric Oxide, CuO.—This black oxide is prepared by igniting copper powder in the air and by ignition of the nitrate and carbonate. Cupric hydroxide loses water slowly at room temperatures, quickly at 100°, with formation of the oxide. This occurs even when the hydroxide is immersed in water:

$$\begin{aligned} 2\ Cu + O_2 &\longrightarrow 2\ CuO, \\ 2\ Cu(NO_3)_2 &\longrightarrow 2\ CuO + 4\ NO_2 + O_2, \\ Cu(OH)_2 &\longrightarrow CuO + H_2O. \end{aligned}$$

Cupric Hydroxide.—This greenish-blue, gelatinous precipitate is formed by addition of a solution of any alkali to a solution of any copper salt:

$$CuSO_4 + 2\ NaOH \longrightarrow Na_2SO_4 + Cu(OH)_2.$$

EXERCISE 1.—Why isn't a precipitate of cupric hydroxide formed in Fehling's solution?

Cupric Sulfide, CuS.—This black sulfide is found in nature as the mineral covellite. It is the most insoluble copper salt we deal with in the laboratory. It can be precipitated from solutions of copper salts by hydrogen sulfide in spite of the presence of concentrated hydrochloric acid. Yet it is attacked by warm nitric acid with formation of the soluble cupric nitrate. The sulfur liberated is converted by continued oxidation into sulfuric acid.

Cupric Sulfate, $CuSO_4$.—This is the copper salt most used. It crystallizes in the rhombic system with five molecules of water as $CuSO_4 \cdot 5\ H_2O$. At 120°–140° it loses four molecules of water, but must be heated to 240° before it loses the fifth molecule of water. The anhydrous salt is white and when crystallized from hot concentrated sulfuric acid exhibits a different crystal form from the "blue vitriol." The anhydrous powder is sometimes used as a dryer for alcohol and such liquids. As it takes up water it turns blue. The term "vitriol" was once applied to any sulfate, and sulfuric acid was termed "oil of vitriol." Ferrous sulfate was green vitriol and zinc sulfate was white vitriol.

Cupric sulfate is made by the action of hot concentrated sulfuric acid on scrap copper. Perhaps copper oxide is first formed for this easily reacts with acid:

$$Cu + H_2SO_4 \longrightarrow CuO + H_2O + SO_2,$$
$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O.$$

On a large scale it is produced by roasting natural sulfides and leaching in the open air with water. Sometimes the copper ores are roasted and treated with sulfuric acid. Copper sulfate is used in calico printing, in electroplating, as a germicide, a fungicide, and as a source of other copper compounds. Bordeaux mixture is made from copper sulfate and calcium hydroxide.

Exercise 2.—Anhydrous cupric bromide, $CuBr_2$, is dark brown. With addition of very little water the color changes through brown to green and with more water to blue. In the light of the ionic theory, what explanation of this color change can you give?

Exercise 3.—Anhydrous cupric chloride is yellow. A concentrated solution is green and a dilute solution blue. Explain.

Ammonia Compounds.—Addition of ammonium hydroxide to a solution of copper sulfate, for example, first yields a green precipitate of basic cupric sulfate, $Cu_2(OH)_2SO_4$, and with an excess of ammonium hydroxide forms the beautiful rich azure-blue solution of the complex cupric ammonia sulfate, $Cu(NH_3)_4SO_4H_2O$. This very soluble salt can be precipitated by addition of alcohol. The soluble complex ionizes as follows:

$$Cu(NH_3)_4SO_4 \rightleftarrows Cu(NH_3)_4^{++} + SO_4^{--}.$$

The $Cu(NH_3)_4^{++}$ ion yields such a low concentration of Cu^{++} ions that many insoluble copper compounds are dissolved by ammonium hydroxide. Even cupric hydroxide is dissolved by ammonium hydroxide, with formation of $Cu(NH_3)_4(OH)_2$. The soluble salts form complex compounds as described for cupric sulfate. Cupric sulfide is the only copper compound not forming a soluble complex with ammonia.

Complex Cyanides.—Attempts to precipitate cupric cyanide fail. It decomposes spontaneously with escape of poisonous cyanogen gas, leaving a precipitate of cuprous cyanide:

$$CuSO_4 + 2\ KCN \longrightarrow K_2SO_4 + Cu(CN)_2,$$
$$2\ Cu(CN)_2 \longrightarrow 2\ CuCN + (CN)_2.$$

With excess of potassium cyanide the insoluble cuprous cyanide dissolves, forming potassium cuprocyanide:

$$CuCN + KCN \longrightarrow K \cdot Cu(CN)_2.$$

The complex negative $Cu(CN)_2^-$ ion yields so few Cu^+ ions that all insoluble copper compounds are dissolved by alkali cyanides. Cupric sulfide is extremely insoluble. Its saturated solution (every precipitate settles from its own saturated solution) contains a minute concentration of Cu^{++} ions, but the complex cyanides of copper yield a still smaller concentration of Cu^{++} ions. Consequently addition of potassium or sodium cyanide to cupric sulfide disturbs every equilibrium in the direction of favoring the existence of the lowest concentration of Cu^{++} ions and the sulfide dissolves. It is worth remembering that most simple cyanides are insoluble but that all complex cyanides are soluble.

Tests for Copper Compounds.—Copper compounds (after moistening with hydrochloric acid to form the volatile chloride) burn with a green flame. Precipitation of the red cupriferrocyanide is a useful test. Usually the peculiar blue color developed when ammonium hydroxide is added to a solution of a copper compound is sufficient indication in analysis. Quantitatively the metal is commonly determined by electrolysis. The copper is plated on a weighed platinum cathode, dried, and weighed.

Exercise 4.—Outline a chapter on copper and briefly discuss the important compounds. Arrange this logically and with the proper sense of proportion, just as if you were writing a book. This is the way to study every metal.

SILVER

Occurrence.—Silver is found free but generally alloyed with gold, copper, or mercury. There are small deposits of horn-silver, $AgCl$, but the principal ore is argentite, Ag_2S, sometimes called silver glance. Lead and copper ores contain some silver, which is recovered in the refining process. Mexico, the United States, Canada, and South America are all leading silver producers; in fact North America furnishes over 70 per cent of the world's silver, which usually totals about 250,000,000 oz. (7,888,000 Kg.) annually.

Metallurgy.—The *amalgamation process* is applicable to ores carrying free silver or to silver chloride. By roasting the sulfide ores with sodium chloride, they yield silver chloride, which can then be amalgamated. Crushed ores treated with mercury yield an amalgam of silver-mercury. This is separated from the waste rock and distilled in an iron retort. The volatile mercury is condensed for further use and the silver is left in the retort. Silver chloride with mercury yields metallic silver by simple displacement and the excess mercury then amalgamates it:

$$AgCl + Hg \longrightarrow Ag + HgCl.$$

The *leaching process* may be applied to the sulfide ores. Silver sulfide is roasted to form the sulfate, which is dissolved by water. Scrap copper added to the solution of silver sulfate displaces the silver and leaves copper sulfate as a valuable by-product:

$$Ag_2SO_4 + Cu \longrightarrow 2\ Ag + CuSO_4.$$

Silver compounds are soluble in alkali cyanides, so ores may be leached with a solution of sodium cyanide. From this solution of the complex cyanide the silver is precipitated by zinc shavings.

✓The *Parkes process* of extracting silver from lead makes use of the principle involved in the extraction of fats from various mixtures by ether. Less than 2 per cent of zinc is melted with the lead. Since silver is far more soluble in zinc than in lead, it is nearly all taken up by the zinc layer floating on top. On cooling the zinc solidifies while the lead is still fluid. The zinc is removed and distilled off from the less volatile silver. On heating the silver in bone ash cupels any lead impurity is oxidized to lead oxide, which is taken up by the bone ash. It should be noted here that most of our silver is a by-product of lead and copper refining, in fact only one-fourth of the world's silver comes from silver mines.

Properties.—Silver is a white metal melting at 962° in absence of air. In the air it melts at 955°, due to the fact that 22 volumes of oxygen dissolve in one volume of molten silver, thus lowering the freezing point. On cooling, this oxygen escapes with a curious spattering of the surface crust. Silver is the best conductor of electricity and but for its cost would displace copper from the electrical industry. Silver is remarkably ductile, having been drawn to wire so fine that 1800 meters weighed 30 g. It is so malleable that foil has been prepared 0.00025 mm. in thickness. It boils at 1955° and has a density of 10.5.

Chemically, silver is inactive. It is not affected by hot oxygen, but is oxidized by moist ozone at 230°. It slowly reacts with sulfur and the halogens. Silver spoons become tarnished with a layer of sulfide when in contact with eggs. A silver coin in contact with a rubber band tarnishes because of the sulfur in the rubber.

Uses of Silver.—Cheaper objects are electroplated with silver by making them the cathodes in a bath of the double cyanide. The plated surface has a frosted appearance until polished. Practically all mirrors are now made by reducing an ammoniacal solution of silver nitrate with glucose, formaldehyde, or Rochelle salts. The reduced silver is deposited on glass and is then varnished to protect it. In earlier days tin amalgam formed the reflecting surface. Silver is much used in coinage, ornaments, and in the preparation of its halogen salts for the photographic industry. One third of all the silver produced in the United States is used to make silver bromide for this industry.

"Oxidized silver" is simply prepared by dipping the metal in water solutions of potassium sulfide or KHS. The thin film of silver sulfide formed is dark, and ornamental when partly rubbed off in spots. "Frosted silver" is prepared by heating a silver copper alloy in air until some copper oxide is formed on the surface. This CuO is then removed by sulfuric acid leaving a surface layer of roughened pure silver.

Silver Oxide.—The oxide is obtained as a brown precipitate when a solution of any alkali is added to a solution of a silver salt. It might be expected that silver hydroxide would be formed, but at least a part of this spontaneously loses water:

$$AgNO_3 + NaOH \longrightarrow NaNO_3 + AgOH,$$
$$2\ AgOH \longrightarrow H_2O + Ag_2O.$$

A suspension of the oxide acts like a strong base, so it must be in equilibrium with some hydroxide in solution. The oxide is decomposed at 250° and is reduced by hydrogen at 100°. Ammonium hydroxide reacts with it to form the soluble complex, $Ag(NH_3)_2OH$. Compare it with copper oxide.

Silver Halides.—These salts are usually formed by addition of a soluble halide to a solution of silver nitrate. The following table is of value in qualitative analysis.

SALT	COLOR	SOLUBILITY	EFFECT OF NH_4OH
AgI	Canary yellow	Most insoluble of the four	Insoluble
AgBr	Yellowish white	Insoluble	Soluble
AgCl	White	Insoluble	Soluble
Ag_2F_2	White	Soluble	——

The chloride and bromide both change in the light, hence their use in photography. Silver iodide is not changed by light unless an excess of silver nitrate is present. The chloride is fairly soluble in concentrated hydrochloric acid, due to the formation of the complex acid H_2AgCl_3. The $AgCl_3^-$ ion yields a lower concentration of Ag^+ ions than is found in a saturated solution of silver chloride. The iodide does not dissolve in ammonium hydroxide because in its saturated solution the concentration of Ag^+ ions is less than that in a solution of the silver ammonia complex ion. With the less insoluble bromide and iodide it is different. The action of ammonium hydroxide on silver compounds is quite similar to its action on copper compounds. The same may be said for the solvent action of potassium cyanide. Sodium thiosulfate dissolves the silver halides because of the formation of a stable complex ion, $Ag(S_2O_3)_2^{--}$:

$$AgCl + 2\ NH_4OH \longrightarrow Ag(NH_3)_2Cl + 2\ H_2O,$$
$$AgCl + 2\ KCN \longrightarrow KCl + K\cdot Ag(CN)_2,$$
$$2\ AgCl + 3\ Na_2S_2O_3 \longrightarrow 2\ NaCl + Na_4Ag_2(S_2O_3)_3.$$

The chemistry of ***photography*** is discussed on page 444 in the chapter on Photochemistry.

Silver Nitrate.—Silver is dissolved by nitric acid with formation of the nitrate:

$$3\ Ag + 4\ HNO_3 \longrightarrow 3\ AgNO_3 + NO + 2\ H_2O.$$

The white crystals of silver nitrate or "lunar caustic" are soluble in water. When pure the nitrate is not affected by light, but reducing agents readily cause formation of black metallic silver. When a solid stick of it is used to cauterize wounds, black stains develop by reduction. Its medicinal value may be due to precipitation of albuminoids.

Ammonium hydroxide is often added to silver nitrate solutions in order to secure the soluble complex ammonia compound. Only small quantities should be used, or if larger quantities are needed they should not be allowed to stand long. Several explosions have occurred, due to the probable formation of an unstable compound of silver and nitrogen.

Exercise 5.—How could you separate the silver from the copper in a silver coin?

Tests for Silver.—The precipitation of white silver chloride, soluble in ammonium hydroxide without blackening, is usually considered a good test for silver compounds. Confirmatory tests may be obtained from the colors of the chromate and phosphate.

Exercise 6.—If silver and its compounds suddenly ceased to exist, could we find adequate substitutes?

Gold

Occurrence.—It is a good thing that gold is not a common metal. Otherwise our monetary standards would be sadly disturbed. We need a rare, inactive, and beautiful metal of not too high a melting point for our standard coins. As it is, the gold production of the world has increased enormously in recent years, thus accounting for part of the increase in price of commodities.

Gold occurs free or alloyed with silver. Its only compound in nature is the telluride, AuTe. The United States produces one-sixth of the world's gold, while the Transvaal of South Africa leads. Australia is third in the list. The world production varies from \$300,000,000 to \$400,000,000 annually. Our dentists require gold to the extent of \$20,000,000 annually. Since Columbus discovered America a billion ounces of gold have been mined, half of it produced in the first 27 years of this present century. North America produced 28 per cent of the billion ounces, Africa 27 per cent and Australasia 17 per cent.

Metallurgy.—Since some gold is found in alluvial deposits, it may be separated by washing in a pan or sluice box. Gold, with its high density of 19.3, settles to the bottom, while the lighter sand, gravel, etc., with an average density of 2.6, is washed away. This is called "placer mining." Sometimes a powerful stream of water is used to force gold-bearing dirt into the sluices. This is "hydraulic mining."

Quartz rock carrying veins of gold is crushed and the material washed over cleats of amalgamated copper. The gold amalgam formed is worked up like the silver amalgam previously described. The tailings of waste rock carry considerable gold, which is leached out by means of sodium cyanide sloution. (See metallurgy of silver.) The oxygen of the air is essential in this process:

$$4\ Au + O_2 + 2\ H_2O + 8\ NaCN \longrightarrow 4\ NaAu(CN)_2 + 4\ NaOH.$$

Gold leaf placed in a bottle filled with boiled sodium cyanide solution does not dissolve, but if a stream of air is led through the solution, the soluble sodium aurocyanide, $Na \cdot Au(CN)_2$, is formed. Commercially the gold is finally secured by electrolysis or by displacement with zinc shavings. Successful reduction with zinc depends upon the partial removal of air:

$$2\ NaAu(CN)_2 + Zn \longrightarrow Na_2Zn(CN)_4 + 2\ Au.$$

EXERCISE 7.—What is the similar reaction in winning silver?

Low-grade ores not worth mining before the introduction of the cyanide process in 1890 have been treated successfully in this way. In South Africa the cyanide method added enormously to the yield of gold, giving us a fine illustration of the relation of chemical reactions to economic conditions.

Properties.—Gold leads the metals in ductility and malleability. Gold leaf has been hammered so thin that it required 110,000 sheets to reach a total thickness of 1 cm. Gold wire has been drawn so fine that 3240 meters weighed only one gram. The element is yellow but the color can be varied by alloying it with silver and the other elements with it. Light transmitted through thin sheets is green. Gold melts at 1063° and volatilizes at temperatures not much higher. It is too soft to be used pure, so coins and jewelry contain copper as a hardening agent. United States gold coins are 90 per cent gold. In jewelry the purity of gold is rated by carats of fineness. Pure gold is 24 carats fine, while the usual jewelry alloy of 18 carats is only 18/24 pure. The specific gravity of pure gold is high, 19.3. Gold is readily obtained in colloidal suspensions that may be red, violet, blue, or green, depending on the size of particle.

Chemically, gold is inactive. Not only is it indifferent to oxygen and hydrogen sulfide, but it resists the attack of nitric acid. However, free chlorine and bromine attack it. Consequently the mixture of concentrated nitric and hydrochloric acids called ***aqua regia*** dissolves gold, forming auric chloride, which, with excess of hydrochloric acid, forms chlorauric acid:

$$AuCl_3 + HCl \longrightarrow H \cdot AuCl_4.$$

The sodium salt of this acid, $NaAuCl_4 \cdot 2\ H_2O$, is used in photography as a toner.

An interesting explanation of the solvent action of aqua regia on gold is given in the *Journal of Chemical Education*, *6*, 533, (1929).

EXERCISES

8. Review all the uses for sodium or potassium cyanide, both analytical and commercial.

9. Why can't we precipitate cupric sulfide from a solution containing considerable potassium cyanide mixed with copper salt?

10. What would we substitute for copper if it were exhausted?

11. What is a test for copper compounds?

12. What is the function of gelatin in photography? Of the hypo?

13. Two grams of silver ore were dissolved in nitric acid and the silver present precipitated with hydrochloric acid. The resulting silver chloride weighed 1.576 g. Calculate the percentage of silver in the ore.

REFERENCES

"The Story of Copper," *J. Chem. Ed.*, *6*, 413, (1929).

"Copper Coating on Glass," *Science*, *66*, 330, (1927). The Eastman Kodak Co. also furnishes working directions.

CHAPTER XLI

MAGNESIUM, ZINC, CADMIUM, MERCURY, AND BERYLLIUM

Second.

The Group.—These elements do not form such a closely-knit family as barium, calcium, and strontium. Zinc and cadmium resemble each other in several respects, but mercury is so different that it is often studied in connection with copper. All the elements of this group are divalent, although mercury forms an additional series of compounds in which its valence is 12

Magnesium

Occurrence.—Magnesium compounds were discovered in 1695 when a spring at Epsom, England, was found to contain magnesium sulfate (hence the name, Epsom salts).

It is a very common element, although not a cheap metal, due to the cost of its preparation. It occurs as magnesite, $MgCO_3$, and as the double salt, dolomite, $MgCO_3 \cdot CaCO_3$. In the Stassfurt deposits it is found as the double chloride, carnallite, $KCl \cdot MgCl_2 \cdot 6\ H_2O$. Meerschaum is $Mg_2Si_3O_8 \cdot 2\ H_2O$ and serpentine $Mg_3Si_2O_7 \cdot 2\ H_2O$. Soapstone, or talc, is $Mg_3H_2(SiO_3)_4$ and asbestos, $CaMg_3(SiO_3)_4$. Epsom Salts -

Preparation.—Davy (1808) isolated the metal in impure form by electrolysis (compare sodium), but Liebig prepared a purer form in 1830 by reducing the chloride with metallic potassium. For a long time reduction with sodium was the commercial, but expensive, method of preparation.

The process in use now is the electrolysis of melted magnesium chloride to which has been added sodium chloride and potassium chloride to lower the melting point. This process is expensive, holding the present cost of magnesium to about 65 cents per pound. Our production in 1928 was 865,666 pounds.

The new American process promised to lower the cost enough to give this important metal very great commercial use but at present it is not in operation. By this process magnesium oxide (prepared by calcining the carbonate) is added to a bath of fused fluorides, principally magnesium fluoride. The oxide is added continuously while the metal is released at the cathode and oxygen at the anodes (burning the carbon anodes to carbon dioxide).

This resembles the Hall process of making aluminum but there are some differences. The magnesium oxide is soluble in the fused bath to the extent of only 0.1 per cent. Perhaps the magnesium fluoride is decomposed into the metal and fluorine, which attacks the oxide.

$$2\ MgO + 2\ F_2 \longrightarrow 2\ MgF_2 + O_2.$$

As this small amount of oxide is used up more dissolves.

Properties.—Magnesium is a silvery-white metal melting at 651° and boiling at 1000°. Its low density of 1.74 is interesting, for there is only one other commercial possibility, aluminum, among the light and strong metals to compete with it as an engineering material and aluminum has a density of 2.70. It is important commercially that magnesium does not rust in dry air. A thin film of hydroxide, turning into the basic carbonate, does form in moist air, but it is coherent enough to protect the metal beneath. Just below its melting point the metal can be drawn into wire. This wire is sometimes rolled into ribbon for special uses.

Magnesium of 99.99 per cent purity can be prepared by sublimation of the crude metal above its melting point of 651° under reduced pressure. The vapor condenses in a beautiful crystalline mass.

One of the chief uses of magnesium is in alloys with aluminum, one of which is called magnalium. These may contain from 8 to 25 per cent magnesium. They are harder, lighter, stronger, and more easily machined than aluminum alone. Another useful alloy contains about 90 per cent of magnesium with some aluminum and copper.

Magnesium alloys are now used in auto pistons, crank cases, forged propellers, amplifying apparatus, in the refining of nickel and in degassing radio tubes.

Chemically, magnesium is a rather active element, since it displaces hydrogen from boiling water. It also has some value in organic syntheses. Magnesium unites with most non-metals. With nitrogen it forms the nitride, Mg_3N_2, of interest because it reacts with water to form ammonia. Magnesium burns at 600°

Aquare

with a brilliant white light, strong in actinic rays, hence its use in flashlight powders. It was much used in star shells for military illumination. Magnesium is not attacked by strong bases while aluminum is, but on the other hand magnesium is attacked by weak acids.

The fact that the metal burns in carbon dioxide shows that it is a powerful reducing agent when hot. In fact it has been used to reduce silicon from its oxides:

$$2\ Mg + CO_2 \longrightarrow 2\ MgO + C,$$
$$SiO_2 + 2\ Mg \longrightarrow 2\ MgO + Si.$$

Magnesium Oxide, MgO.—This white oxide is obtained by heating the carbonate ($MgCO_3 \longrightarrow MgO + CO_2$). The reaction occurs at a lower temperature than that of a limekiln. Like calcium oxide, this oxide unites with water to form the hydroxide but not with the evolution of as much heat. Its chief use is as a refractory lining for high-temperature furnaces. If the carbonate be used as a lining, it is turned into the oxide during use by the heat of the furnace.

Magnesium Hydroxide, $Mg(OH)_2$.—This compound is white and rather insoluble, so a suspension of it in water is used medicinally to neutralize undue acidity of the stomach and as a laxative. As fast as the small amount in solution reacts with acid more precipitate dissolves, so a small and harmless concentration of OH⁻ ions is maintained until all the precipitate is dissolved.

basic

Magnesium Chloride, $MgCl_2$.—This salt is found in salt brines and is a by-product in separating potassium chloride from carnallite at Stassfurt. When heated sufficiently the crystallized salt, $MgCl_2 \cdot 6\ H_2O$, is hydrolyzed completely by its own water of crystallization (favored by rise in temperature):

$$MgCl_2 \cdot 6\ H_2O \longrightarrow MgO + 5\ H_2O + 2\ HCl.$$

This reaction shows the danger from the use of sea water in boilers. The acid released attacks the metal of the boiler. It will be possible to make all the hydrochloric acid we need by heating crystallized magnesium chloride. The anhydrous salt can be prepared by heating carefully the double salt $MgCl_2 \cdot NH_4Cl \cdot 6\ H_2O$. The water is driven off first and then the ammonium chloride volatilized. The crystallized salt is used as a filler for cotton and woolen goods and in making *magnesia cements.* A wet mixture of the oxide and chloride hardens with formation of the basic chloride. Sawdust or wood meal is added as a filler. Such compounds make wall plasters or floorings, or stucco for outside walls. Of course any filler may be added.

Magnesium Carbonate, $MgCO_3$.—This salt occurs as the mineral magnesite in Greece, Austria, the United States, and other countries. It was imported into this country, until the World War, for furnace linings because the domestic product was unsuitable. When our importations were shut off our open-hearth steel furnaces and copper converters suffered. Finally it was proved that the foreign product had just enough iron oxide in it to give it the necessary wearing quality, while our own was too pure. Straightway enough iron oxide was mixed with Washington magnesite to give it the same quality. The deposits in Washington and California are extensive. In 1928 these deposits yielded 127,000 tons, and we imported nearly 150,000 tons, chiefly from Austria.

The normal carbonate cannot be obtained by precipitation with a solution of sodium carbonate. Instead, a basic salt is formed, its composition varying with the temperature and other conditions. The hydrolysis of sodium carbonate yields OH^- ions as well as CO_3^{--} and, since magnesium hydroxide is even more insoluble than the carbonate, the conditions favor formation of a basic salt such as $3\ MgCO_3 \cdot Mg(OH)_2 \cdot 3\ H_2O$. This is sold as "magnesia alba" and used in cosmetics or in tooth powders. A crude product of loose fibrous structure is sold as "magnesia pipe covering" for heat insulation of steam pipes. In this field it is a rival of asbestos.

Heat Insulation. Asbestos interwoven with wire serves the automobile industry as a brake lining but it is as a heat insulator around boilers and steam pipes that it is most useful. Mixed with portland cement it is converted into fire-proof asbestos-shingle roofs.

Magnesium Sulfate, $MgSO_4$.—There are deposits of magnesium sulfate in the western states and at Stassfurt. When crystallized from solution at ordinary temperatures the heptahydrate, $MgSO_4 \cdot 7\ H_2O$, is secured. This is sold as Epsom salts. The various hydrates lose water at 200°. Magnesium sulfate is used in dyeing, tanning, as a filler for cotton goods, and in medicine.

Magnesium Ammonium Phosphate, $MgNH_4PO_4$.—When any soluble orthophosphate is added to a solution of a magnesium salt with ammonium hydroxide and any ammonium salt a fine, crystalline precipitate of $MgNH_4PO_4$ is obtained. When ignited it forms the very stable pyrophosphate, $Mg_2P_2O_7$. This reaction is the basis of the quantitative determination of phosphates in fertilizers, etc.:

$$Na_2HPO_4 + MgCl_2 + NH_4OH \longrightarrow 2\ NaCl + H_2O + MgNH_4PO_4.$$

A reagent called ***magnesia mixture*** is used in this precipitation. It might seem impossible to prepare a solution containing both Mg^{++} ions and OH^- ions (from $MgCl_2 + NH_4OH$) and, in fact, if nothing else were added this mixture would form a precipitate of magnesium hydroxide. But the addition of any ammonium salt prevents precipitation. Ammonium hydroxide is a weak base and its ionization is greatly suppressed by the mass action of a great excess of NH_4^+ ions from the well-ionized ammonium chloride:

$$\begin{aligned}(1)\quad NH_4OH &\rightleftarrows NH_4^+ + OH^-,\\ (2)\quad NH_4Cl &\rightleftarrows NH_4^+ + Cl^-.\end{aligned}$$

The equilibrium in (1) is driven so far to the left that the concentration of OH^- ions left is very small, too small with the Mg^{++} ions present to exceed the solubility product of magnesium hydroxide. It is even possible to dissolve a precipitate of the hydroxide by addition of an ammonium salt. It is evident that the following equilibria must exist in a water suspension of magnesium hydroxide:

$$\begin{aligned}\text{Undissolved } Mg(OH)_2 &\rightleftarrows \text{dissolved } Mg(OH)_2\\ &\rightleftarrows Mg^{++} + OH^- + OH^-.\end{aligned}$$

Removal of OH^- ions, whether by addition of H^+ ions from an acid or NH_4^+ ions from ammonium chloride must disturb all equilibria continuously to the right, with final solution of the precipitate.

Magnesium Perchlorate, $Mg(ClO_4)_2$.—This salt ("dehydrite") when prepared in anhydrous and granular form is a powerful drying agent, taking up 30 per cent its own weight of water vapor.

Tests.—The best test for magnesium compounds is the precipitation of the crystalline magnesium ammonium phosphate as described above.

Exercise 1.—In what localities do you expect to find the metal magnesium manufactured?

Zinc

Occurrence.—The world produced 1,330,000 tons of smelter zinc in 1927 and of this the United States accounted for nearly one-half. It is found in every state, although only twenty-three states are producers. The Missouri-Kansas-Oklahoma field leads, with lead sulfide-zinc sulfide ores. New Jersey is second with a unique mixture of oxides of zinc, iron, and manganese called franklinite and a zinc silicate called willemite. Some zincite, the simple oxide, is found there. New Jersey boasts of the largest zinc mine in the world, producing 2000 tons of ore daily. Montana is next in order of importance, with the ores at Butte. Wisconsin, Colorado, and Idaho are large producers. Sphalerite or zinc blende, ZnS, and smithsonite, $ZnCO_3$, are the chief ores in the western United States.

The ancients did not know zinc as a free metal, but produced brass by smelting zinc ores with copper. The Chinese isolated the element in the sixth century but Europe made no progress with it until the eighteenth century.

Metallurgy.—Many zinc ores need to be concentrated before smelting can be profitable, so the oil-flotation process is used as with copper sulfide ores. Oxides or carbonates need only roasting with coal to reduce them to the metal. Sulfides must be roasted with excess air to secure the oxide of zinc, which is then further roasted with carbon to secure reduction. In some smelters a sulfuric acid plant is attached to utilize the sulfur dioxide:

$$2\,ZnS + 3\,O_2 \longrightarrow 2\,ZnO + 2\,SO_2,$$
$$ZnO + C \longrightarrow Zn + CO.$$

The zinc oxide and coal are heated in fire-clay retorts. The zinc is volatilized and then condensed in receiving vessels. Carbon monoxide burns at the mouth of each receiver. Since zinc boils at 925° and the temperature of the reduction is about 1200°, it is evident that the vapor of the metal must be formed. When the vapors are led into cold receivers at any temperature below 415° (melting point of zinc), only zinc dust is obtained, but as the hot vapors heat the receivers above 415° only the liquid form is condensed. This is cast into slabs called spelter. It may be purified by electrolysis. (See Copper.)

Properties of Zinc.—Zinc is a blue-white metal whose properties vary with its treatment. Cast zinc is hard and brittle, but if heated to 100°–150° it becomes so malleable that it can be rolled to thin sheets, which remain soft and malleable on cooling to ordinary temperatures. The density of cast zinc is 6.93 and of rolled zinc 7.18. The melting point is sometimes given as 415°, but varies above or below this according to the physical history of the sample. Zinc tarnishes in the air with formation of a film of basic carbonate. When very hot it reacts with steam:

$$Zn + H_2O \longrightarrow ZnO + H_2.$$

It burns in air with a bluish flame and formation of white fumes of the oxide. It is the most active of the cheap metals, so it is made the "dissolving element" of most primary cells, yet pure zinc is scarcely attacked by dilute sulfuric acid. The presence of another metal or impurity, less active, causes a rapid attack of the zinc by the acid, although the bubbles of hydrogen are released on the surface of the other metal. Zinc dust particles are usually covered with a film of oxide. On exposure to moist air large quantities of zinc dust in storage have been known to take fire.

Uses of Zinc.—The most important use of the metal is in galvanizing iron to protect the iron from rusting. As zinc itself does not rust, the iron beneath cannot be attacked until the zinc surface is scratched or broken. Then with both metals in contact with moist carbon dioxide of the air we have a galvanic battery with solution of the more active metal, zinc. Later the iron is attacked. Galvanizing is done by cleaning the rust or scale from iron with dilute sulfuric acid and dipping the clean iron into melted zinc. On cooling the zinc crystallizes in the familiar spangled design. At least 2 oz. per square foot of surface are needed to give protection Another method of applying a zinc surface to iron is *sherardizing.* The iron wire or sheet is covered with zinc dust and baked at a temperature approaching 800°. The zinc penetrates the iron to some extent. By the *Schoop* process a spray of melted zinc is atomized with a blast of air or other gas. This spray of minute drops coats any object, wood, metal, paper, etc., with a coherent layer of zinc.

Rolled zinc is used for roofing, gutters, washing machine parts, and battery elements. Alloyed with copper it forms brass, one of the most useful of all alloys. Zinc dust is a valuable reducing agent in organic syntheses. Zinc salts are poisonous, so food containers should not be made from this metal. Zinc shavings are used to displace gold and silver from the cyanide solutions employed in metallurgy.

Zinc Oxide, ZnO.—This white solid has been made by burning the metal (French process) but most of it is prepared by direct roasting of the ores (direct process) with a large excess of air. The dust is caught in bags which allow gases to go through. The oxide is yellow when hot, but pure white when cold. Artists use the best grade of it under the name, "Chinese white." Ground with linseed oil, it forms one of the best white paints. It is especially good for laboratories because hydrogen sulfide cannot change its color in forming white zinc sulfide. Painters now prefer an addition of from 5 to 35 per cent basic lead sulfate to zinc oxide in paints.

The greatest demand for zinc oxide, however, is as a filler in rubber goods, especially automobile tires. It is mixed with gutta percha and Venice turpentine to make surgeon's adhesive tape. As a filler in oilcloth, celluloid, and glazes it is important. Zinc oxide mixed with phosphoric acid sets quickly to a strong dental cement. It has some use in face powders and in wall papers.

Zinc Hydroxide, $Zn(OH)_2$.—This white insoluble compound is readily formed by union of the Zn^{++} ion of any soluble zinc salt with the OH^- ions of any strong base:

$$ZnSO_4 + 2\ NaOH \longrightarrow Na_2SO_4 + Zn(OH)_2.$$

It is an *amphoteric* hydroxide acting like an acid and a base. It is dissolved by a strong acid, which leads us to call it a base, but it is also dissolved by a strong base, so we are forced to call it an acid:

$$Zn(OH)_2 + 2\ HCl \longrightarrow 2\ H_2O + ZnCl_2,$$
$$Zn(OH)_2 + 2\ NaOH \longrightarrow 2\ H_2O + Na_2ZnO_2.$$

Sodium zincate, $Zn(ONa)_2$ or Na_2ZnO_2, is a soluble salt. Zinc hydroxide evidently forms both H^+ ions and OH^- ions in water. The truth is, some molecules ionize one way and some the other:

$$Zn(OH)_2 \rightleftarrows Zn^{++} + OH^- + OH^-,$$
$$Zn(OH)_2 \rightleftarrows H^+ + H^+ + ZnO_2^{--}.$$

Why not invent the term, "zincic acid" and write the equation

$$H_2ZnO_2 \rightleftarrows H^+ + H^+ + ZnO_2^{--}?$$

The student may ask here how $Zn(OH)_2$ can ionize at all if it is insoluble. All compounds have some solubility, even if very minute in some instances. The very small amount of zinc hydroxide in solution is in equilibrium with its own ions and with the undissolved hydroxide:

$$\begin{tikzcd}
 & Zn^{++} + OH^- + OH^- \arrow[d, shift right] \\
\text{Undissolved } Zn(OH)_2 \arrow[r, shift left] & \text{dissolved } Zn(OH)_2 \arrow[l, shift left] \arrow[u, shift right] \arrow[d, shift right] \\
 & H^+ + H^+ + ZnO_2^{--} \arrow[u, shift right]
\end{tikzcd}$$

When an excess of H^+ ions from a strong acid is added, the OH^- ions are removed as water and every equilibrium disturbed in the direction of basic ionization. The entire precipitate is converted into zinc chloride or some such salt. On the other hand if an excess of OH^- ions is added (strong base), the H^+ ions will be removed and every equilibrium disturbed in the direction of the acid ionization. All the precipitate is converted into some soluble salt, such as sodium zincate. It has been suggested that $Zn(OH)_2$, or H_2ZnO_2, ionizes into H^+ and $HZnO_2^-$ (a monobasic acid).

Zinc hydroxide also dissolves in an excess of ammonium hydroxide, not because of the formation of ammonium zincate, but because of the formation of the soluble complex base, $Zn(NH_3)_4(OH)_2$. The concentration of simple Zn^{++} ions derived from further ionization of the $Zn(NH_3)_4^{++}$ ion is lower than it is in a saturated solution of zinc hydroxide.

Exercise 2.—If ammonium zincate could be formed in any way, how would it react in aqueous solution? Why?

Zinc Chloride, $ZnCl_2$.—This very soluble salt can be made by the action of hydrochloric acid on the metal, the oxide, or the carbonate. As a salt of a weak base and a strong acid, it is hydrolyzed, yielding an acid solution. It melts at 290° and on cooling forms a very solid mass. It has a strong affinity for water and is very caustic. It is much used as a timber preservative in railway ties and trestle work. It slowly digests cellulose to a soft gelatinous mass that may be molded into various shapes. After washing out the zinc chloride and drying we have fiber board, fiber buckets, etc., all light, strong, and resilient. Pails must be varnished to make them waterproof. A wet mixture of zinc chloride and zinc oxide sets to a solid cement of the basic chloride. In this respect zinc resembles magnesium.

Zinc Sulfide, ZnS.—As the mineral sphalerite, zinc sulfide is yellow to black, but the pure precipitated compound is white (the only white sulfide). When roasted to a very moderate temperature it may be converted into the sulfate, but at higher temperatures it becomes the oxide. In the laboratory precipitation is secured by union of Zn^{++} ions and S^{--} ions. The sulfide ions may be from hydrogen sulfide or ammonium sulfide:

$$(1) \quad ZnCl_2 + H_2S \rightleftarrows ZnS + 2\ HCl,$$
$$(2) \quad ZnCl_2 + (NH_4)_2S \longrightarrow ZnS + 2\ NH_4Cl.$$

In reaction (1) there is a serious difficulty. At first the concentration of S^{--} ions from the hydrogen sulfide may be sufficient, with the Zn^{++} ions, to exceed the solubility product of zinc sulfide.

$$[Zn^{++}] \times [S^{--}] = K, \text{ solubility product.}$$

But hydrochloric acid is formed as a by-product and its high concentration of H^+ ions greatly represses the slight ionization of hydrogen sulfide. Consequently very soon the S^{--} ion concentration falls so low that the solubility product of zinc sulfide is no longer exceeded and no further precipitation occurs. To be sure, addition of some other ion that would remove the offending H^+ ions of the hydrochloric acid would permit precipitation. A strong base with its OH^- ions could do this. So could sodium acetate, with its acetate ions which tie up most of the H^+ ions in the form of weakly ionized acetic acid:

$$H^+ + C_2H_3O_2^- \rightleftarrows H \cdot C_2H_3O_2.$$

Reaction (2) is favored because *salts* of hydrogen sulfide ionize freely and also because there is no acid formed to repress any essential ionization. So it is clear that zinc sulfide can be precipitated by passing hydrogen sulfide into a solution of any zinc salt containing sufficient sodium acetate or by use of any soluble sulfide other than hydrogen sulfide.

Lithopone.—This important pigment has been mentioned in connection with barium sulfide. It is made by mixing solutions of barium sulfide and zinc sulfate:

$$BaS + ZnSO_4 \rightarrow BaSO_4 + ZnS.$$

Both products are white and insoluble. The precipitate first formed has no body or hiding power, but when washed, dried, heated to dull redness, suddenly quenched in cold water, ground wet, washed, and dried again, it yields an excellent pigment. Lithopone is a brilliant white with better hiding power than zinc oxide. It is unexcelled for interior painting, for first coats, floor oilcloth, and several other uses. Curiously enough it darkens slightly in sunlight, but after a night's rest is as white as ever. This renewal is perpetual.

Research has improved the quality in this respect so much that we now use 150,000 tons of lithopone per year.

Tests.—The characteristic white color of zinc sulfide precipitated from solutions of zinc salts or zincates by ammonium sulfide is a test for the metal. Any zinc compound moistened with a solution of cobalt nitrate and heated on charcoal gives a green stain (Rinmann's green).

Exercise 3.—Why is zinc not used as a structural metal in the place of steel?

Zinc Chart

- Zinc Ore
  - Zinc Oxide
    - Paint
    - Pharmaceuticals
    - Rubber
      - Tires and Tubes
      - Rubber Foot Wear
      - Rubber Clothing
      - Surgical Rubber Goods
      - Mechanical Rubber Goods
    - Celluloid
    - Oilcloth
    - Printing Ink
    - Glue
    - Glass
    - Glazes
  - Metallic Zinc
    - Rolled Zinc
    - Galvanizing
      - Roofing
      - Gutters
      - Leaders
      - Weather Strips
      - Washing Machines
      - Boiler Plates
      - Battery Cells
      - Apparatus and Instrument
      - Hardware
      - Sheets, Tubes, and Rods
      - Lighting Fixtures
      - Castings
      - Bronzes
    - Brass
  - Lithopone
    - Linoleum
    - Flat Wall Paints
    - Window Shades

CADMIUM

Occurrence and Preparation.—Cadmium occurs in small quantities in zinc ores. Being more volatile than zinc it is found in the first distillate, from which it can be separated by fractional redistillation (in an atmosphere of hydrogen to prevent oxidation). Western zinc spelter carries about 0.4 per cent cadmium. It does some harm, but the cost of removal is discouraging.

Properties.—Cadium looks much like zinc, melts at 321°, boils at 778°, and has a density of 8.64. Its chief use has been in low-melting alloys, such as those used for automatic fire sprinklers and electric fuse wires. Some cadmium is also used for special solders and bearing metals. Its use is growing rapidly in several important alloys, as a white foundation for silver plating, and as a rival to nickel plate. The 1927 production was 1,000,000 pounds.

Cadmium Sulfide, CdS.—The most important compound of cadmium is cadmium sulfide. It is a very permanent bright yellow and is used as a pigment under the name "cadmium yellow." The sulfide occurs as the mineral greenockite and is precipitated, even in weakly acid solutions, by union of Cd^{++} ions and S^{--} ions. However, it dissolves in sufficiently strong acid, so it is best to precipitate in concentrations of acid not exceeding 0.5 N HCl.

Tests.—The yellow color of cadmium sulfide is a distinctive test when separated from arsenic compounds. It differs from copper with which it is grouped in qualitative analysis in that the complex cadmocyanide yields enough Cd^{++} ions to allow precipitation of cadmium sulfide by hydrogen sulfide, while the similar complex cuprocyanide does not yield enough Cu^{++} ions to permit precipitation of the very insoluble copper sulfide.

MERCURY

Occurrence and Metallurgy.—Because of the simplicity of its metallurgy, mercury has long been known. The alchemists were fascinated by its properties and attached great mysteries to it. To some extent it occurs free, but most of the world's mercury is obtained from the red sulfide, cinnabar, HgS. This is found in Italy, Spain, Austria, Mexico, the United States, and Japan. Our domestic deposits are found in California and Texas, with a little in Oregon. Of the world's production of 5000 tons the United States produced only 422 tons in 1927, yet this country once produced 2000 tons annually.

The sulfide ore is roasted in air and the volatile mercury condensed. Any mercuric oxide formed would be decomposed at the roasting temperature:

$$HgS + O_2 \longrightarrow Hg + SO_2.$$

It is the commercial custom to sell the metal in iron flasks containing 75 pounds.

To purify the metal for accurate laboratory use it is usually allowed to fall in minute drops through a depth of two meters of dilute ferric chloride or nitric acid (density of 1.1) to oxidize any impurities. The nitric acid is contained in a long tube with the lower end drawn out and bent like a U. The bend of the U is kept filled with pure mercury, and any additional amount overflows into a receiver. To secure a spray of mercury a funnel is worked in the flame until a slight flange on the stem is formed and a bag of coarse canvas or chamois tied over this flange. In running through the cloth the metal is broken into many fine streams (Fig. 145).

Properties.—Mercury is a beautiful silvery liquid at ordinary temperatures; in fact it is the only metal liquid under such conditions. Cæsium comes near it. Mercury freezes at − 39.4°, boils at 357°, and has a high density, 13.596 at 0°. It has a noticeable vapor tension at ordinary temperatures. A gold leaf suspended above the mercury in a bottle turns white eventually. When heated well above its boiling point, the vapor conducts electricity quite well, with radiation of a bluish-green light rich in ultra-violet rays. Lamps using this principle are made of glass tubes when only the visible light is desired, but when the ultra-violet rays are wanted for water sterilization, the tube must be of clear quartz. Glass stops ultra-violet rays, while quartz lets them through.

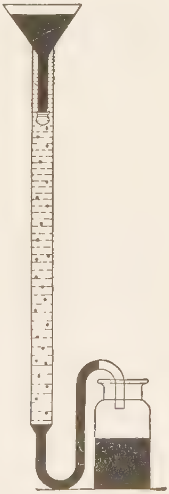

FIG. 145.—Purifying mercury.

Mercury is used in thermometers, air pumps, gas measuring and collecting, and was once essential to the manufacture of mirrors. Now all mirrors have a silver reflecting surface. Mercury forms amalgams with nearly all metals. It does not wet platinum or iron. The formation of amalgams with gold and silver is important in their metallurgy. Silver and gold amalgams are used in filling teeth. An amalgam of sodium and mercury (formed with the evolution of much heat) is useful as a reducing agent. The mercury dilutes the sodium, so the violence of its action on water is greatly lessened. Such an amalgam containing only 3 per cent of sodium is quite solid. Sodium and mercury form a definite series of compounds.

Chemically, mercury is almost a "noble" metal. It is oxidized slowly by air only above 300°, as Lavoisier learned in his classic experiment (page 26). However, it unites readily with sulfur and the halogens. Simple grinding of mercury and sulfur in the mortar produces some black mercuric sulfide. Mercury is not attacked by any acids except the oxidizing ones, such as nitric and hot concentrated sulfuric acid. The metal is not poisonous in the mass, but all its soluble salts are, as is the vapor.

A new development in power generation holds wonderful possibilities for the mercury industry if it proves successful. The mercury boiler uses mercury instead of water in a boiler. The gaseous mercury is allowed to expand through a turbine and finally all returned to the first boiler as liquid mercury. The last of the hot exhaust is used to generate steam for a special turbine. A much greater temperature range is secured than with steam alone. A fuel saving of 50 per cent seems possible but there are difficulties.

Unfortunately the first commercial boiler equipped holds 15 tons of mercury and the world's annual production could equip only 300 such boilers.

Mercury Poisoning.—The possibility of utilizing mercury in boilers for power generation calls attention to the accompanying possibility of leaks in the boiler or pipes involved. Mercury vapor is far too poisonous for such mischance and so its presence in air must be readily recognized by some delicate test. Such a test is now possible in the darkening of properly prepared selenious sulfide paper. By using colorimetric standards and varying the time of exposure this indicates the presence of mercury in the air to the extent of one part in 8,000,000 (or 20,000,000 of air, according to some investigators).

Some alarm has been raised by the statements of Stock, an eminent German chemist, that enough mercury vapor is formed from exposed surfaces of liquid mercury used in laboratories to undermine the health of laboratory workers. Good ventilation and reasonable precautions should greatly lessen this hazard, if it really exists.

MERCUROUS COMPOUNDS

Mercurous Oxide, Hg_2O.—Addition of sodium hydroxide to a solution of any mercurous salt yields a black-brown precipitate of the oxide. This is very unstable in the light and on moderate heating:

$$Hg_2O \longrightarrow Hg + HgO.$$

Mercurous Chloride, HgCl.—This insoluble white substance is used medicinally under the name ***calomel.*** It stimulates the liver and other glands. It is prepared by subliming mercury mixed with mercuric chloride:

$$HgCl_2 + Hg \rightleftarrows 2\ HgCl.$$

This reaction is slightly reversible so the poisonous mercuric chloride must be washed out of the sublimate with alcohol or water. Medical men are careful to remember that light decomposes mercurous chloride ($2\ HgCl \longrightarrow Hg + HgCl_2$) forming some of the extremely poisonous mercuric chloride. Consequently they always keep calomel in dark bottles. The white chloride blackens in contact with ammonia. The color is due to the finely divided metal:

$$2\ HgCl + 2\ NH_3 \longrightarrow NH_4Cl + Hg + Hg(NH_2)Cl.$$

Mercurous Nitrate, $HgNO_3 \cdot H_2O$.—This is the most important soluble mercurous salt. It is obtained by the action of cold dilute nitric acid on excess mercury. Since mercury does not displace hydrogen from acids, the first step must be the formation of the oxide, which then reacts with the excess nitric acid. Mercurous nitrate is hydrolyzed to such an extent that some nitric acid must be added to prevent precipitation of the basic salt, $Hg_2(OH)NO_3$. Some free mercury must also be present to reduce any mercuric ions formed by oxidation:

$$Hg + Hg^{++} \longrightarrow 2\ Hg^{+}.$$

Mercurous Sulfate, Hg_2SO_4.—This white, slightly soluble salt is prepared in a manner analogous to that for mercurous nitrate. An excess of mercury is treated with sulfuric acid. Its chief use is in the standard cells for electrical measurements.

MERCURIC COMPOUNDS

Mercuric Oxide, HgO.—Lavoisier made this red substance by heating mercury in air at 300°–350°. This method is too slow, so usually it is prepared by heating dry mercuric nitrate with mercury. (See preparation of nitrogen dioxide.)

$$Hg(NO_3)_2 + Hg \longrightarrow 2\ HgO + 2\ NO_2.$$

If sodium hydroxide is added to a mercuric salt solution, a yellow form of the oxide, HgO, is precipitated. The hydroxide has never been isolated. The yellow form is composed of smaller crystals than the red and is more active. As Priestley taught the world, mercuric oxide, heated to a temperature well above 350°, releases oxygen.

Mercuric Chloride, $HgCl_2$.—Mercury unites with chlorine with a green flame and production of mercuric chloride, but the usual method of preparation is to heat a mixture of mercuric sulfate and sodium chloride. A crystalline sublimate is secured:

$$HgSO_4 + 2\ NaCl \longrightarrow HgCl_2 + Na_2SO_4.$$

A little manganese dioxide may be added before subliming in order to oxidize any mercurous sulfate formed. The sublimate melts at 288° and boils at 303°. It is somewhat soluble in cold water but much more so in hot water. Mercuric chloride forms more soluble complex salts with sodium or potassium chloride, such as $K_2HgCl_4 \cdot H_2O$. The simple salt is very poorly ionized, differing from the nitrate. In 0.1 N solutions the chloride is only one per cent ionized and yields no precipitate with potassium dichromate. On the other hand mercuric nitrate in 0.1 N solution is 10 per cent ionized and yields a precipitate with this reagent.

This salt is extremely poisonous and is known to the public as *corrosive sublimate*. Since it coagulates albumen, the white of egg is the proper antidote.

Mercuric Iodide, HgI_2.—Mercuric iodide is formed as a yellow precipitate, instantly changing to scarlet, when Hg^{++} ions and I^- ions are brought together. When heated above 126° the red modification turns yellow. On cooling below 126° the yellow form may persist but on being scratched with some hard object it suddenly reverts to the red form. Similar color changes are found with some of the double iodides. With an excess of potassium iodide the soluble complex salt, $K_2 \cdot HgI_4$, is formed. Such a solution contains too low a concentration of simple Hg^{++} ions to yield a precipitate of the oxide on addition of potassium hydroxide. Such a mixture of the complex salt and alkali is known as Nessler's solution. It is especially useful in analysis to detect and determine ammonium compounds. With ammonia a yellow color or even a precipitate is formed.

Temperature color changes of the double iodides of mercury -copper and mercury-silver may be utilized to indicate overheating of machinery parts. A surface painted over with the former changes from bright red to dark brown at 71° C. and to black at 100° C. On cooling the red appears again. The silver-mercury salt changes from yellow to dark orange or brick red at 71° C.

Question.—If a vertical stripe of one of these pigments were painted on the outside of a hot water tank, how could you readily read the level of the water?

Mercuric Nitrate, $Hg(NO_3)_2$.—This is a colorless, soluble salt produced by completely dissolving mercury in an excess of hot nitric acid. (Compare with mercurous nitrate.) Its solution is very acid by hydrolysis.

Mercuric Sulfate, $HgSO_4$.—By heating mercury in concentrated sulfuric acid ***mercuric sulfate*** is formed.

Only brief mention may be made of the other mercuric salts. ***Mercury fulminate,*** $Hg(ONC)_2$, is the detonating charge used to set off high explosives. ***Mercuric sulfide*** is very insoluble, yet it is dissolved by a solution of sodium sulfide.

$$HgS + Na_2S \longrightarrow Hg(SNa)_2.$$

Tests.—Precipitation of the white mercurous chloride which turns black with ammonia is the usual test for mercurous salts.

Mercuric salts are detected by formation of the black sulfide, which is then converted into mercuric chloride by aqua regia and reduced by stannous chloride:

$$\begin{aligned} 2\ HgCl_2 + SnCl_2 &\longrightarrow 2\ HgCl + SnCl_4, \\ 2\ HgCl + SnCl_2 &\longrightarrow 2\ Hg + SnCl_4. \end{aligned}$$

At first the white calomel is precipitated and later this is completely reduced to the black finely divided mercury.

Exercise 4.—What is the new fluoride process of preparing magnesium by electrolysis?

Exercise 5.—What are the uses of magnesite, $MgCO_3$?

Exercise 6.—How can you mix Mg^{++} ions and OH^- ions in the same solution without getting the usual precipitate of $Mg(OH)_2$?

Exercise 7.—Why doesn't hydrogen sulfide precipitate all the Zn^{++} from a solution of zinc chloride?

Exercise 8.—How does the mercury boiler work?

Exercise 9.—At 400° the vapor density of mercurous chloride indicates a decomposition into two molecules. We might assume that

$$Hg_2Cl_2 \rightleftarrows 2\ HgCl,$$

but a gold leaf exposed to the hot vapors is quickly amalgamated. Amalgams are alloys of mercury and another metal. What really happened above?

Beryllium

Beryllium, Be (or *Glucinum* Gl), occurs in the mineral beryl, a beryllium aluminum silicate. When this is transparent and tinted green with chromium silicate, it is called emerald. Wöhler prepared the element in 1828 by heating the chloride with potassium. It decomposes hot water slowly and reacts readily with dilute acids and dilute alkalies.

Beryllium is a light gray metal, capable of taking a high polish, hard enough to scratch glass, four times as elastic as aluminum but only two-thirds as heavy, and almost as elastic as steel. Chemically it resembles aluminum and alloys with it, but as a metal it strongly resembles silicon. Its density is about 1.84 and its melting point 1260° C., near which temperature it oxidizes readily in the air.

Of course its low density and its alloying qualities make beryllium interesting but the present cost is a bar to its extensive use. In 1922 it sold (a few grams of it) at $5,000 per pound, in 1929 at about $100.00 per pound, and now we are promised a probable reduction to $10.00 or less per pound. One of the pioneering methods of manufacturing involves the electrolysis of a fused mixture of barium beryllium fluoride with sodium beryllium fluoride, using a hollow water-cooled iron cathode and a graphite crucible as anode, but there are other methods. Unfortunately the temperature of these baths must be above the melting point of beryllium, 1260°. The ores, once thought rare, are really plentiful, in fact there is as much beryllium in the earth as lead or zinc.

To aluminum the element adds strength and resistance to corrosion; to copper and iron it adds hardness; but it does not alloy at all with magnesium. Undoubtedly beryllium alloys have a future in aircraft construction. The alloys with iron, copper and nickel are improved by heat treatments.

As a window in X-ray tubes beryllium transmits the rays seventeen times as well as the usual aluminum window, because of its lower atomic weight.

Question.—What are the three light metals suited to engineering work?

Beryllium Hydroxide, $Be(OH)_2$.—The hydroxide of beryllium is white, gelatinous and amphoteric, thus closely resembling zinc hydroxide. Its salts are strongly hydrolyzed. The older name, *glucinum,* was given because of the sweetish taste of the soluble salts.

EXERCISES

10. A man bought 90 kg. of mercuric chloride, but received, by mistake, mercurous chloride. Being a chemist, he converted it into mercuric chloride. How much mercuric chloride did he gain by the mistake?

11. What weight of magnesite will be required in the preparation of 125 g. of magnesium oxide.

12. How much mercury and sulfur dioxide can be obtained from 0.57 metric tons of cinnabar (60 per cent pure)?

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CHAPTER XLII

ELECTROCHEMISTRY

Ionic Displacement.—Zinc dust, shaken with a solution of copper sulfate, removes the blue color with evolution of heat. After filtering, metallic copper is found on the filter and a solution of zinc sulfate in the filtrate. In other words, blue copper ions have become red copper molecules; and zinc molecules have become zinc ions. Equation (2) gives the essentials of equation (1):

$$\text{(1)}\quad Zn + Cu^{++} + SO_4^{--} \longrightarrow Cu + Zn^{++} + SO_4^{--},$$
$$\text{(2)}\quad Zn + Cu^{++} \longrightarrow Cu + Zn^{++}.$$

Essentially,

$$Zn \longrightarrow Zn^{++} + 2(-),$$

and

$$Cu^{++} + 2(-) \longrightarrow Cu$$

where 2(—) represents two electrons lost or gained. Apparently, the zinc atom is better able to take or hold positive charges than is the copper atom. In reality the zinc atom in gaining two positive charges has given away two electrons (negative charges of electricity) to the copper ion. Loss of electrons by a metallic atom means the formation of a positive ion. A number of other displacement reactions have already been observed by the student. The displacement of hydrogen from acids is especially familiar:

$$Zn + 2\,H^{+} \longrightarrow Zn^{++} + H_2,$$
$$Zn + 2\,Ag^{+} \longrightarrow Zn^{++} + 2\,Ag,$$
$$Fe + Cu^{++} \longrightarrow Fe^{++} + Cu.$$

Evidently a displacement series of the metals can be arranged in which a given metal will displace from salt solutions any metal below it, but will in turn be displaced by any metal above it. Such a series has a number of names. It was given on page 83 as the "activity series" with the most active metals at the top. Now we see that those at the top have the greatest tendency to lose electrons—to go into solution as ions. Hence the name, "solution tension series." For reasons to be made clear later, it is also called the "electromotive series." An abbreviated list of the metals in proper order follows:

MOST ACTIVE
K
Na
Ca
Mg
Al
Zn
Fe
Ni
Sn
Pb
H
Cu
Hg
Ag
Pt
Au
LEAST ACTIVE

Electric Cells.—When a strip of zinc is placed in a solution of copper sulfate all the energy of the reaction is evolved as heat. There is no current of electricity, that is, no flow of electrons along a wire or other circuit. The copper ions come in direct contact with the metallic zinc. However, if they are kept apart by a suitable device, the same reaction may take place but with the important difference that nearly all the energy is released as electricity. Solutions of zinc sulfate and copper sulfate may be kept apart by a porous clay wall which permits ions to wander through when attracted but hinders ordinary diffusion (Fig. 146). A zinc plate is placed in the sinc sulfate compartment and a copper plate in the copper sulfate compartment. On connecting the two plates by a wire a current of electrons flows along the wire from zinc to copper and through the solutions to the zinc. This device is a primary cell (as differing from a secondary or storage cell) and converts chemical energy into electrical energy. The zinc, with a greater solution tension, or pressure, than the copper, throws atoms into solution as ions. This means that some zinc atoms give up electrons to the rest of the zinc plate. These electrons flow along the wire (current of negative electricity) to the copper plate, where they are readily taken up by the adjoining copper ions. This action neutralizes the charge on the copper ions and causes a deposition of metallic copper on the plate. The zinc plate is finally dissolved and the copper ions all removed. The excess Zn^{++} ions attract SO_4^{--} from the other compartment, so all portions of the solutions are kept electrically neutral.

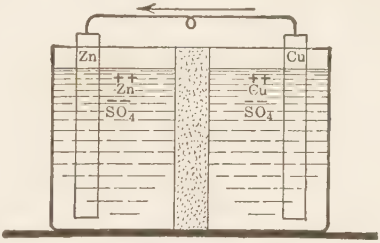

FIG. 146.—A primary cell.

Many such cells are possible. In fact, any two metals in a solution of any electrolyte may be connected as a cell somewhat similar in action to the one just described. In all cases the more active metal dissolves. The direction of the current, as arbitrarily named, is opposite to the flow of electrons along the wire. This decision as to the direction of flow was made before scientists knew anything about electrons.

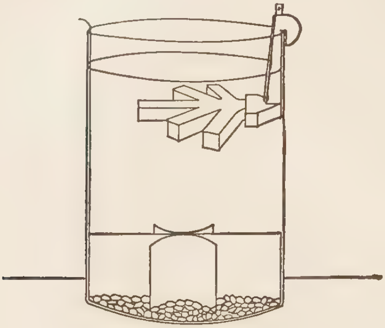

Fig. 147.—The gravity cell.

The Gravity Cell (Fig. 147) is a convenient arrangement of the zinc-copper cell. The copper plate lies in a saturated solution of copper sulfate, while the zinc plate (shaped like a crowfoot) is hung over the edge of the jar in the lighter solution of zinc sulfate or dilute sulfuric acid. Thus gravity helps to keep the two solutions apart without a diaphragm. This battery, in either form, is often called the Daniell cell.

Electromotive Force.—The force that drives the electrons along a metallic circuit is termed ***electromotive force*** (E. M. F.) or voltage and its unit of measurement is the volt. The difference in this pressure or potential between the two poles of a Daniell cell is 1.10 volts. Other cells, such as the Clark and Weston, are better standards. If a cell is made of two metals close together in the electromotive series, the voltage is very low. The farther apart they are in the series the higher the voltage.

Normal Potentials.—Any metal in water or water solution has a tendency to throw atoms into solution as ions. There is an actual solution pressure differing in degree with the position of the metal in the activity series. In the case of zinc immersed in a solution of a zinc salt (that is, in a solution already containing Zn^{++} ions) the tendency of the neutral zinc atoms on the surface of the plate to give up electrons to the rest of the plate is opposed by the tendency of Zn^{++} ions to take up electrons from the plate. With such an active metal as zinc the former tendency is the greater and the metal plate soon becomes negative from the electron donations while the solution with a certain excess of Zn^{++} ions becomes positive with respect to the plate. A difference of electric potential is set up. Of course, the greater the concentration of the Zn^{++} ions in solution, the greater the tendency of Zn^{++} to take electrons from the plate and the positive potential of the plate is lessened.

With the less active metals like copper in a solution of a copper salt the concentration is generally sufficient to make the tendency of Cu^{++} ions to take on electrons from the atoms of the plate greater than the opposing tendency and the copper plate actually becomes negative with respect to the solution.

$$\begin{aligned} Zn &\rightleftarrows Zn^{++} + 2(-), \\ Cu &\rightleftarrows Cu^{++} + 2(-). \end{aligned}$$

Fused salts are usually supposed to ionize well, yet it is possible that in some of their mixtures one salt may ionize well in a solvent of another salt poorly ionized, or that poorly ionized complex salts may form.

Even hydrogen gas in contact with a conducting electrode like platinum has a tendency to ionize, to donate electrons to the obliging platinum electrode, making it negative. However, in a solution of H^+ ions, an acid solution, this tendency is opposed by that of the H^+ ions already there to take on electrons from this same platinum plate.

$$H_2 \rightleftarrows 2H^+ + 2(-).$$

We elect to use this potential of the hydrogen electrode under standard conditions, hydrogen gas on the surface of a platinum electrode immersed in a normal solution of H^+ ions (some suitable acid), as a standard of comparison for other electrode potentials. A stream of hydrogen gas must keep the solution saturated with hydrogen molecules at one atmosphere pressure.

The Hydrogen Electrode.—Different single electrodes have been set up with known potentials. A standard often used is the calomel electrode in which metallic mercury is the pole in contact with a saturated solution of mercurous chloride (calomel) and is connected with the other half of the battery by a wire from the metal and a conducting liquid path of a tube filled with some salt such as potassium chloride (a salt bridge). Under certain conditions the single potential of this calomel electrode is known exactly. When connected with another half cell of unknown potential it is possible by passing the resulting current through a potentiometer and measuring the net potential of the whole system to calculate the potential of the second electrode.

The hydrogen electrode already described is merely a sheet of platinum with a roughened surface of platinum black saturated with hydrogen gas by a steady stream of the gas, immersed in a solution containing hydrogen ions and in contact with an atmosphere of hydrogen gas. Of course, the voltage or potential varies with the concentration of the H^+ ions. With an acid solution of known concentration this half cell becomes a standard cell, with known potential. Joined to a standard calomel electrode for the other half cell, it furnishes a combination whose net potential is the algebraic difference between the two electrode potentials.

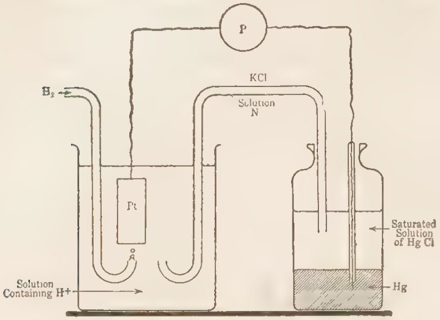

FIG. 148.—The hydrogen electrode.

Using the unknown solutions as the liquid to surround another platinum black electrode also joined to a second standard calomel electrode, the potential developed by this cell may be compared with that developed in the other.

The H^+ ion concentration of the unknown acid solution is then readily calculated and usually stated as the pH value (p. 228).

Purely for convenience the potential of hydrogen against a N solution of its own ions is taken as zero. In the table below, the metals with a greater tendency than hydrogen to give up electrons to the neutral metal plate are marked with a negative sign because the neutral plate thus becomes negatively charged with electrons donated.

POTENTIALS OF METALS IN CONTACT WITH N SOLUTIONS

(Electromotive Series)

Li	−3.02	Cr (Cr^{++})	−0.6(?)	Sb	+0.1(?)
K	−2.92	Cr (Cr^{+++})	−0.5(?)	Bi	+0.2(?)
Na	−2.72	Fe (Fe^{++})	−0.43	As	+0.3(?)
Ba	−2.8(?)	Cd	−0.40	Cu (Cu^{++})	+0.34
Ca	−2.5(?)	Ni (Ni^{++})	−0.22	Cu (Cu^{+})	+0.51
Mg	−1.55	Sn (Sn^{++})	−0.14	Hg (Hg^{+})	+0.79
Al	−1.34	Pb (Pb^{++})	−0.13	Ag	+0.80
Mn (Mn^{++})	−1.0(?)	Fe (Fe^{+++})	−0.04	Hg (Hg^{++})	+0.86
Zn	−0.76	H_2	0.00	Au (Au^{+})	+1.5(?)

It is, of course, easier to discharge metallic ions on platinum than on more active metal cathodes in electrolysis because the solution pressure of the platinum itself is so small. Yet when the platinum becomes covered with a layer of hydrogen gas as sometimes happens, the discharge is no longer against a platinum plate but against a hydrogen plate. That is why the voltage or potential difference in a dry cell falls with steady use. However, the cell is packed with manganese dioxide which in the resting periods of this common type of primary cell slowly oxidizes the troublesome film of hydrogen and "depolarizes" the battery. It is interesting to note here that over 500,000,000 of these dry batteries are used in the United States every year.

When an unknown acid surrounding the platinum black electrode is to be titrated with a standard base the end point is accurately recognized by a critical change in the potential of the cell. After calculating pH values from the potentials, they may be plotted against the volumes of standard base solutions added.

In Fig. 149 is represented the three-step neutralization of phosphoric acid by potassium hydroxide. Formation of KH_2PO_4 or K_2HPO_4 or K_3PO_4 can be controlled and recognized at will as desired.

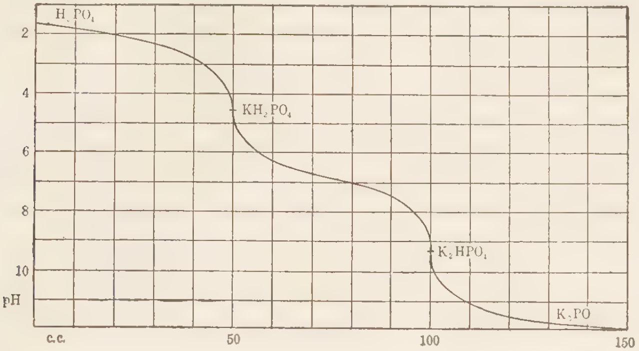

Fig. 149.—Electrometric titration curve showing the change in the pH value of a solution of H_3PO_4 during the addition of KOH solution.

From a table of potentials the voltage of any combination may be calculated. It is merely the difference in potential between the two elements. For example, the voltage of the Daniell cell (Cu − Zn) is $+ 0.34 - (- 0.76) = 1.10$ volts.

Exercise 1.—What is the voltage of the Pb-Pt cell?

It is interesting to learn that the voltage of a Daniell cell can be radically changed by adding ammonia to reduce the concentration of Cu^{++} ions. Potassium cyanide reduces the concentration so much that the copper plate actually goes into solution (solution tension exceeds osmotic pressure) and the action of the cell is reversed. Zinc is deposited.

Electric Energy.—Electric energy is measured by the product of the intensity factor times the quantity factor. The volt is the unit of intensity and the coulomb the unit of quantity. Since the flow of water in a pipe leading from an elevated reservoir is somewhat comparable to the flow of electricity, we may consider the difference in electric potential between any two points in a circuit as analogous to the difference in "head" or pressure of water at the reservoir and at the open tap. The unit of actual quantity of water is the gallon, no matter what the pressure or rate of flow. The coulomb is likewise a unit of actual quantity of electricity. A gallon of water delivered under a definite pressure delivers a definite amount of energy to a water motor. So a coulomb of electricity delivered under a certain voltage or electrical pressure delivers a definite number of joules of energy:

$$1 \text{ volt} \times 1 \text{ coulomb} = 1 \text{ joule}$$
$$1 \text{ joule} = 0.24 \text{ cal.}$$

A simple definition of the coulomb may be taken from the fact that 96,500 coulombs of electricity will discharge one gram-equivalent weight of any ion during electrolysis. When one gram-equivalent weight of zinc displaces copper from a solution of a copper salt, 25,050 cal. of heat are liberated.

Exercise 2.—Calculate how many coulombs are delivered in a Daniell cell when one gram-equivalent weight of zinc is dissolved. Give the heat equivalent of the electrical energy evolved.

The ***rate*** of delivery of a given number of joules is important. One coulomb per second means a current strength of one ***ampere*** (similar to one gallon of water per second). The unit of rate of delivery is the ***watt:***

$$1 \text{ ampere} \times 1 \text{ volt} = 1 \text{ joule per sec.} = 1 \text{ watt.}$$

The horsepower is 746 watts (about as much energy as a common electric iron uses). A 40-watt lamp on a 110-volt circuit must use a 0.36 ampere current:

$$x \text{ amperes} \times 110 \text{ volts} = 40 \text{ watts,}$$
$$x = 0.36 \text{ ampere.}$$

Through any cross section of the filament in a 15-watt tungsten lamp there pass one billion times one billion electrons every second.

Electric energy is sold by the kilowatt (1000 watts) hour.

Oxidation and Reduction.—Loss of electrons from a metallic atom or ion is oxidation, while gain of electrons is reduction. The zinc atom is oxidized in becoming the zinc ion and the Fe^{++} ion is oxidized in becoming the Fe^{+++} ion. In the Daniell cell the general effect is the oxidation of zinc atoms by Cu^{++} ions. When this oxidation and reduction occur at the same point heat is evolved, but when they occur at two different points, as in an electric cell, the energy appears as a current of electricity.

This oxidation and reduction can be demonstrated clearly by the use of a salt bridge (Fig. 150). In one beaker is a solution of ferrous chloride and in the other a solution of sodium chloride and chlorine. An inverted U-tube filled with sodium chloride solution connects the two beakers. The platinum poles are connected by a wire. The Fe^{++} ions give one electron to the platinum pole, thus becoming Fe^{+++} ions. These electrons flow along the wire to the platinum pole in the other beaker, where they are taken up by chlorine atoms. These Cl^- ions then travel through the U-tube, attracted by the excess of positive charges of the Fe^{+++} ions. Thus ferrous chloride is oxidized by chlorine, which never comes in contact with the iron salt.

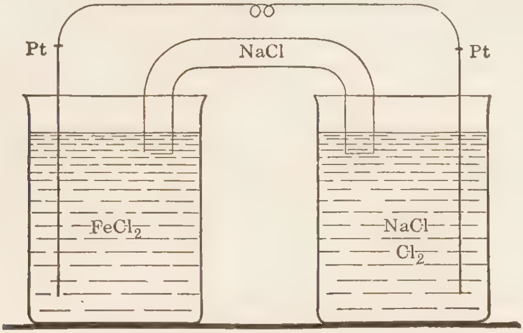

Fig. 150.—Oxidation at a distance.

EXERCISES

3. What is the source of the current in a Daniell cell?

4. A certain electric iron uses 50 watts on a 110-volt circuit. How much will the current cost at 8 cents per kilowatt-hour if the iron is used continuously for three hours?

5. How much silver will be deposited by a current of 1.5 amperes in 45 minutes?

6. If zinc costs $0.15 per kilogram, what would it cost per kilowatt hour to draw current from a Daniell cell, ignoring the cost of the copper sulfate? How does this compare with the rate in your town?

7. How much electrical energy would be obtained when 150 g. zinc dissolve in a Daniell cell?

8. What will be the voltage of the following cells: Zn–Pb; Pb–Ag; Cu–Au; Sn–Hg; Pt–H?

9. When a hydrogen electrode is connected with a chlorine electrode to form a cell a current flows. Why? Is the platinum pole in water saturated with chlorine gas negative or positive?

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CHAPTER XLIII

ALUMINUM. DYES. CEMENT

Occurrence.—Aluminum is the most extensively distributed of the metals, making up about 7 per cent of the earth's crust. It never occurs free, but nearly all rocks except sandstone and limestone contain aluminum compounds. Such silicates as feldspar, $KAlSi_3O_8$, and mica, $KAlSiO_4$, are common. Ordinary clay, $H_2Al_2(SiO_4)_2 \cdot 2\ H_2O$, cryolite, Na_3AlF_6, bauxite, $Al_2O_3 \cdot 2\ H_2O$, and corundum, Al_2O_3, are well-known compounds of aluminum.

Preparation.—Aluminum is the latest of the great commercial metals to come into common use. This was due largely to the difficulty of reduction of its oxide. Wöhler was the first to produce it (1827) although the Danes have lately brought from long-buried archives evidence that Oerstedt actually made very crude aluminum in 1825. Wöhler heated the anhydrous chloride with metallic potassium:

$$AlCl_3 + 3\ K \longrightarrow Al + 3\ KCl.$$

This method, yielding a metal that sold for $160 per pound, was not destined to make aluminum compete with anything but museum specimens. The French chemist, Deville, improved the process in 1854 by using the cheaper sodium instead of potassium and the less volatile double chloride of sodium and aluminum instead of the simple chloride. The price fell to $15 per pound. Castner, ~~the American~~, attempted to cheapen aluminum by cheapening sodium and in this he succeeded in 1886. His work forced aluminum down to $4 per pound. A large sodium plant was erected for the new industry, but just then Castner's plans were upset by Hall's wonderful discovery in 1886. Nothing daunted, Castner went ahead and invented the highly successful Castner cell for producing sodium hydroxide by electrolysis of sodium chloride.

Charles M. Hall, a student in Oberlin College, attacked the problem of making cleap aluminum and succeeded where the greatest scientists of the century had failed. It occurred to him that if he could find an easily melted mineral in which aluminum oxide dissolved, the solution might be electrolyzed. Such a rock he found in cryolite, 3 NaF · AlF_3, from Greenland. Hall secured his electric current from all the batteries he could borrow or make. By melting the cryolite in a graphite crucible with the heat of a charcoal furnace and using a carbon anode, he managed to secure a few buttons of the precious metal, the best one of which is on exhibition in the Severance Laboratory of Oberlin College. Within a few months after his graduation (in 1886) this youth of twenty-two years laid the foundation for a great industry. It is interesting to know that only a few months later the young Frenchman, Heroult, duplicated Hall's discovery quite independently. Hall had the usual inventor's troubles in getting a market for his ideas, but by 1890 his company was producing aluminum commercially (Fig. 151). The price fell to 18 cents per pound in 1914, but of course rose somewhat during the war. The production had grown rapidly, but the World War stimulated the demand beyond all previous records. In 1928 the United States produced 160,000,000 pounds, while the entire world produced 450,000,000 pounds. In addition, 88,000,000 pounds of old scrap was remelted and used in this country alone. Hall's original company is still the sole producer in this country, not because of patents, for they have expired, but because of possession of the best ore deposits and perfection of manufacturing operations. The best bauxite deposits in the world were supposed to be in France, but the American company secured control of a vast deposit in British Guiana that is purer than French ore. Dutch Guiana is now producing more than the neighboring British colony. Previously the supply was secured mainly from Arkansas, although Georgia, Tennessee, and Alabama also produced. This original company is now developing one million

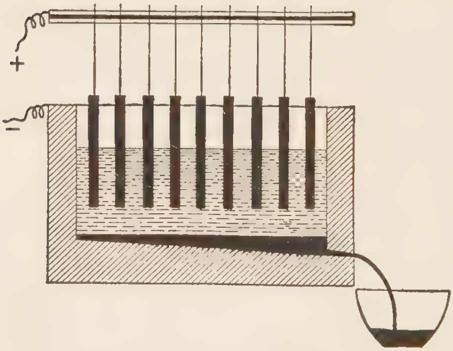


Fig. 151.—The Hall electrolytic process of making aluminum.

horsepower on the Saguenay river in Quebec. The aluminum industry of America will probably center at this waterfall.

Most bauxite contains iron oxide as an impurity. This is removed by digesting the ore with concentrated sodium hydroxide under steam pressure which dissolves the aluminum as sodium aluminate but does not attack the iron oxide. This solution is then diluted and treated with freshly precipitated aluminum hydroxide which, in settling, drags down the greater portion of the original dissolved aluminum hydroxide. Aluminum hydroxide is also precipitated by carbon dioxide.

The ignited hydroxide (now alumina, Al_2O_3) is added to the cell ready for electrolysis. These cells are iron boxes lined with a tarry material (retort coke). About 40 carbon anodes dip into the bath, which is kept molten (at 900°–1000°) merely by the heat of resistance. The iron cell is the cathode. The metal is discharged at the cathode and sinks to the bottom, to be tapped off from time to time. Oxygen is evolved at the anodes. Since it is only the dissolved alumina that is decomposed, the cryolite should never need renewal—but it does. Calcium fluoride, aluminum fluoride, and the chlorides of sodium, potassium, and aluminum may now be added to improve the bath. The potential fall in a cell is only about five volts, but a flow of several thousand amperes is maintained.

Other methods of separating pure alumina from crude bauxite have been developed. Most of them depend upon electric furnace heating of the ore mixed with coke to reduce oxides of iron, silicon and titanium, while the aluminum oxide remains unreduced.

Properties.—The metal aluminum is the lightest of all the very common metals, its density being only 2.6, while iron is three times as heavy. In color it somewhat resembles silver, but with a bluish light. It melts at 658° and boils at 1800°. It is rolled or hammered most easily at 100°–150°. Near the melting point it is so brittle that it can be ground to a powder. It is an excellent conductor of heat and electricity. In wire of the same cross section it conducts electricity only two-thirds as well as copper, but weight for weight it excels copper in this respect. More than 250,000 miles of such cables are in use. Only iron and copper among the pure metals have greater tensile strength.

Chemically aluminum is very active, yet it is tarnished only slightly in air. This is due to the formation of a thin coherent film of the oxide which protects the metal beneath. Hydrochloric acid dissolves it readily ~~with escape~~ of hydrogen, but cold dilute nitric acid attacks it slowly. This is probably due to the oxidizing action of nitric acid. When aluminum is wet with dilute solution of mercuric chloride, mercury is displaced (why?) and at once forms an amalgam with the aluminum. This amalgamated aluminum rapidly displaces hydrogen from water while the insoluble hydroxide forms, so it is best to keep mercury salts away from aluminum. Like zinc this metal is dissolved by solutions of sodium or potassium hydroxide:

$$2\ \mathrm{Al} + 6\ \mathrm{NaOH} \longrightarrow 2\ \mathrm{Al(ONa)_3} + 3\ \mathrm{H_2}.$$

Uses of Aluminum.—Because it is light, strong, and not noticeably corroded in air aluminum has many commercial uses. It is next in tonnage after iron, copper, zinc, and lead, and in twenty years will rank next to copper. It is now used in large quantities to remove air bubbles from steel ingots at the moment of pouring. The light aluminum oxide formed floats to the top. Aluminum is much used for auto parts, the rigid structure of airships and structural work of various kinds. The powdered metal is mixed with oil or a volatile liquid and used as a paint for radiators and other metallic articles. Aluminum paint is largely used as a covering for oil storage tanks in order to reflect much of the sun's heat radiation and thus lessen the usual losses of volatile constituents such as gasoline. In the form of cooking utensils it has a merited popularity. Since its salts are not poisonous the thin foil is coming into use as a food wrapper. The alloy with magnesium, called magnalium, is stronger and is machined more readily than aluminum itself. Aluminum cannot be turned easily in a lathe. The golden bronze containing 92 per cent copper and 8 per cent aluminum is now much used for gears in auto trucks and for other ~~purposes~~ where toughness, resistance to abrasion, and corrosion ~~are~~ important. These proportions are varied widely and small percentages of other elements added. Some modern alloys of this type have the advantage of strength approaching that of steel, great hardness, resistance to corrosion, beauty, susceptibility to high polish and lightness. Finally, such bronzes can be cast while steel cannot. In all probability the greatest future of aluminum lies in the direction of alloy making. Street cars, furniture, shingles are now being made from aluminum or its alloys.

Duralumin, the greatest of all aluminum alloys, containing 95.5 per cent aluminum, 3 per cent copper, 1 per cent manganese, and 0.5 per cent magnesium, is much used for airplane, airship, and auto structure. It has the strength of steel with about one third of its weight. Heat-treatment of aluminum alloys greatly improves them.

Steel-cored aluminum wires for long-distance power transmission at high voltages are rapidly coming into more general use.

A remarkable alloy of aluminum containing 13 per cent silicon is "modified" in structure by the addition of a fraction of one per cent sodium just before casting. This refinement gives the alloy high strength and durability due to the greater uniformity of structure. Recently the effort to give aluminum a harder and more attractive surface by plating with nickel and then with chromium has succeeded. With earlier efforts the plate failed to adhere during the usual wear.

Of our aluminum	
The auto industry uses	30%
Other transportation industries	10%
Electric cable	15%
Cooking utensils	15%
Radio and elec. appliances in household	8%
Non-ferrous metal industries	8%
Steel ingots	5%
Machine and appliances	5%
Miscellaneous	4%
	100%

"Aluminothermy" is a process developed by Goldschmidt, who discovered that powdered aluminum when ignited reduces many metallic oxides with evolution of a great amount of heat (Fig. 152). Temperatures of 3000° are obtained so the molten metal may be cast in a mold:

$$Fe_2O_3 + 2\,Al \rightarrow Al_2O_3 + 2\,Fe.$$

The heat of formation of Al_2O_3 is 392,600 cal., while the heat of decomposition of Fe_2O_3 is 197,000 cal. so 195,600 cal. are freed. If a shaft on a ship at sea had been broken, the ends could be welded together by surrounding them with a sand or clay mold and igniting a mixture of iron oxide and aluminum powder (thermit) is a funnel above. The melted iron runs into the mold, melts the broken ends of the shaft, and produces a perfect union. In actual practice the shaft ends are preheated.

Since the heat of formation of magnesium oxide is greater than that of a comparable amount of aluminum oxide it is evident that aluminum will not reduce magnesium oxide.

Large charges of thermit have been used successfully in loosening dangerous ice jams in rivers. In one instance a million ton ice jam was removed in nine hours by the use of two 90 lb. charges of thermit. Of course the heat developed is localized, but when the ice structure is weakened at critical points the whole mass moves. Attempts have been made to shatter icebergs.

An aluminum dust blowpipe has just been devised. A cloud of fine metal dust is blown through the lamp with oxygen, igniting readily to give a terrifically hot flame. The high heat of formation of Al_2O_3 explains it.

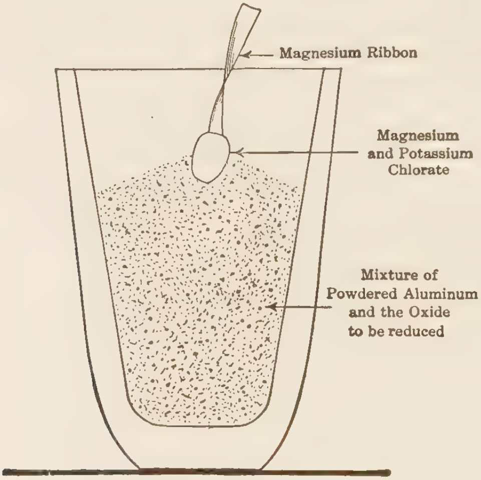

Magnesium Ribbon
Magnesium and Potassium Chlorate
Mixture of Powdered Aluminum and the Oxide to be reduced

FIG. 152.—The thermit process.

Aluminum of High Purity.—The best commercial grade of this metal had averaged close to 99.5 per cent, rarely higher, but the Hoopes process of electrolytic purification has recently given the world aluminum as pure as 99.983 per cent. In this process a layer of the molten aluminum alloyed with copper and some silicon as anode is covered by a lighter layer of molten salts of aluminum, sodium, and barium fluoride. The pure aluminum cathode layer (in contact with graphite electrodes) grows on top of the molten salts and is poured off from time to time. This pure metal has a beautiful silver color (which it retains), in contrast to the bluish tint of common commercial aluminum.

Su~~ccess in~~ rolling thin layers of this purest aluminum on sheets of duralumin has added greatly to the usefulness of this great alloy. Salt spray from the ocean as well as other atmospheric influences, caused a dangerous weakening of duralumin through intercrystalline corrosion starting at the surface. The "Alclad" sheets (duralumin surfaced with the pure metal), promise to prevent this corrosion and to extend the life and use of such alloys. The purest metal has superior resistance to corrosion. Since the pure metal is electro-negative to the alloy beneath it exerts an electrolytic as well as mechanical protection at scratches, cracks and exposed edges.

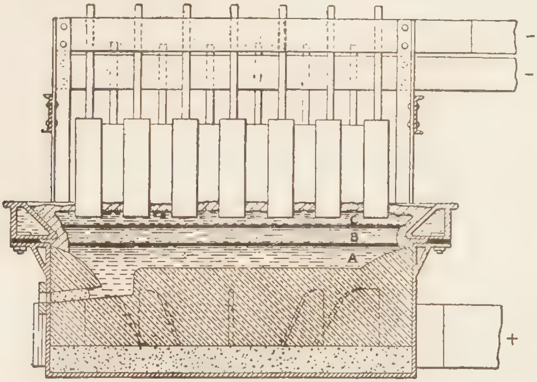


Fig. 153.—Hoopes cell for electrolytic refining of aluminum. In the lower half of the cell, at A, is the molten anode alloy. Upon this is superimposed the molten bath B, while at C is the molten aluminum cathode, floating on the bath.

Aluminum Oxide, Al_2O_3.—The mineral bauxite may be considered as the partly dehydrated hydroxide or the hydrated oxide. Corundum is an impure form of the oxide, extremely hard, hence the variety known as emery is used as an abracive or polishing material. Emery contains some iron oxide. The mineral bauxite is heated until portions fuse and then ground to a powder. This is really artificial corundum and is used as an abrasive under the name alundum. Countless parts of an automobile are finished by grinding. The chemists and metallurgists have been continually making tougher and harder steels which can not be satisfactorily machined, but must be shaped by grinding. Abrasives are of service not alone as grinding wheels. Loose abrasives are used, suspended in grease or water, for grinding valves, for lapping piston pins and rings, crankshaft pins and bearings, etc.

The gems, ruby and sapphire, are crystals of pure corundum colored by traces of other metallic oxides.

Artificial Gems.—Artificial rubies and sapphires are now manufactured that are in every way the equal of the natural gems, chemically and artistically. When powdered ammonium alum, $NH_4Al(SO_4)_2 \cdot 12H_2O$, is sifted through an oxyhydrogen flame it melts. The drops are caught on a very small support and finally build up a "boule" of Al_2O_3 in the shape of an inverted chestnut. Ammonia and sulfur trioxide are volatilized with the water of the alum. This boule looks like a clear glass but in reality it has a crystalline structure. It is cut and polished, yielding beautiful "white sapphires." If a little chrome alum, $NH_4Cr(SO_4)_2 \cdot 12\ H_2O$, is crystallized with the other alum, the chromium oxide formed as an impurity changes the white sapphire to a magnificent ruby. This may be pink or deep red, depending on the amount of chromium oxide present up to 2.5 per cent of chromium oxide. A pigeon blood ruby worth several hundred dollars can be duplicated for a few dollars. Yet not exactly duplicated, for under the microscope the minute bubbles in the artificial ruby are found to be rounded, while those in the natural gem are flat sided. The blue color of sapphires is obtained by the use of a trace of titanium oxide.

Wade's interesting little book, *Precious Stones* (Putnam and Sons), is worth reading.

Aluminum Hydroxide, $Al(OH)_3$.—This white, insoluble hydroxide is precipitated when any ~~soluble base~~ is added to a solution of an aluminum salt; in other words, by the union of Al^{+++} ions with OH^- ions:

$$AlCl_3 + 3\ NaOH \longrightarrow Al(OH)_3 + 3\ NaCl.$$

That it is a basic hydroxide is clearly shown by the fact that many acids dissolve it:

$$Al(OH)_3 + 3\ HCl \longrightarrow AlCl_3 + 3\ H_2O.$$

That it is an acid is just as clearly shown by the startling fact that sodium and potassium hydroxides dissolve it:

$$Al(OH)_3 + 3\ NaOH \longrightarrow Al(ONa)_3 + 3\ H_2O.$$

There is but one explanation. Aluminum hydroxide is amphoteric, some molecules ionizing as an acid and some as a base. If the objection is raised that this hydroxide is insoluble, it can be pointed out that a very small amount is really in solution, and in equilibrium with the undissolved phase:

$$\underset{\text{Undissolved}}{Al(OH)_3} \rightleftarrows \underset{\text{Dissolved}}{Al(OH)_3} \begin{array}{l} \rightleftarrows Al^{+++} + OH^- + OH^- + OH^- \\ \rightleftarrows H^+ + H^+ + H^+ + AlO^{3---} \end{array}.$$

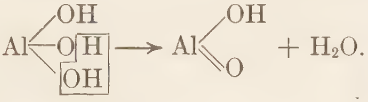
These equilibria may be disturbed in one direction by addition of an excess of OH^- ions or in another direction by addition of an excess of H^+ ions. (Compare with zinc hydroxide.)

With weak bases or weak acids, aluminum hydroxide forms no salts. For instance, the carbonates and sulfides of many metals are precipitated from solution, but these salts of aluminum are not so precipitated. If aluminum sulfide, Al_2S_3, is formed by direct union of the heated elements and then added to water, it is completely hydrolyzed, with precipitation of the hydroxide:

$$Al_2S_3 + 6\ H_2O \longrightarrow 2\ Al(OH)_3 + 3\ H_2S.$$

In fact, any attempt to precipitate aluminum sulfide by adding ammonium sulfide to a solution of an aluminum salt results only in precipitation of the hydroxide.

When it acts as an acid, aluminum hydroxide is called aluminic acid, H_3AlO_3, and its salts aluminates, such as Na_3AlO_3. By loss of water metaluminic acid, $HAlO_2$, may form. The most stable aluminates at high temperatures are the salts of the meta-acid:



Aluminum Chloride, $AlCl_3$.—When aluminum or its hydroxide is dissolved in hydrochloric acid and the solution concentrated, crystals of the chloride, $AlCl_3 \cdot 6\ H_2O$, are formed. Any attempt to secure the useful anhydrous salt by driving off the water fails. With rise in temperature hydrolysis increases, so that only the oxide and hydrochloric acid are formed:

$$2\ AlCl_3 + 3\ H_2O \longrightarrow Al_2O_3 + 6\ HCl.$$

This reaction is really reversible and the water could be removed safely in a stream of dry hydrogen chloride. By mass action this would push the equilibrium to the left and yet remove the water. In actual practice it is simpler to leave water out of the situation. Dry chlorine, or even hydrogen chloride not quite dry, is passed through a tube containing hot aluminum. Aluminum chloride sublimes:

$$2\ Al + 3\ Cl_2 \longrightarrow 2\ AlCl_3,$$
$$2\ Al + 6\ HCl \longrightarrow 2\ AlCl_3 + 3\ H_2.$$

The anhydrous salt is very useful in some organic reactions. It fumes strongly in moist air, due to hydrolysis.

Since the MacAfee process of cracking petroleum oils under atmospheric pressure by heating with anhydrous aluminum chloride is now established commercially, it is essential that the cost of the aluminum chloride be low. In 1929 a single plant produced 75,000 pounds daily at less than 5 cents per pound from bauxite, chlorine and coal. The bauxite, roasted at 1000° to convert it to aluminum oxide, is next mixed with coal until coal distillation products escape and finally heated with chlorine (the coke furnishing the heat) to convert the aluminum oxide into anhydrous aluminum chloride which distills off.

Double Salts.—When certain salts are mixed in proper proportions and the solution concentrated slowly, crystals appear containing both salts in a very definite proportion. These are called double salts. The alums are good examples:

$$K_2SO_4 + Al_2(SO_4)_3 + 24\ H_2O \longrightarrow K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\ H_2O.$$

In dilute solution these double salts yield the simple ions of their constituent salts. However some salts on mixing form compounds which do not yield all the simple ions again. These are called *complex salts:*

$$Fe(CN)_2 + 4\ KCN \longrightarrow K_4Fe(CN)_6,$$
$$K_4Fe(CN)_6 \rightleftarrows 4\ K^+ + Fe(CN)_6^{----}.$$

The potassium ferrocyanide mentioned here yields no simple iron ions, but instead the complex ferrocyanide ion. A similar complex ion of cadmocyanide breaks down to a slight extent, yielding some simple cadmium ions, but much of the complex still remains.

The Alums.—Common alum, $KAl(SO_4)_2 \cdot 12\ H_2O$, may be formed as above or by merely mixing solutions of potassium sulfate and aluminum sulfate in molecular proportions. On concentration the solution yields octahedral crystals. There are some deposits of a basic alum known as alunite in Utah, Italy, Hungary, and many other places. Because many substituted alums are possible by replacing potassium with almost any monovalent metal (Na, Cs, Rb, Ag, NH_4), this is sometimes distinguished as "potash alum." Still further substitution is possible, in that any trivalent metal may be used in place of aluminum. These all crystallize with twelve molecules of water and all have the same characteristic crystalline form. Consequently crystals containing a number of alums are possible or layers of one may form around another. Below are given some of the best known alums:

$NaAl(SO_4)_2 \cdot 12\ H_2O$, Soda alum
$NH_4Al(SO_4)_2 \cdot 12\ H_2O$, Ammonium alum
$KFe(SO_4)_2 \cdot 12\ H_2O$, Iron alum
$NH_4 \cdot Cr(SO_4)_2 \cdot 12\ H_2O$, Ammonium chrome alum.

Exercise 1.—Why isn't the double sulfate formed by mixing solutions of ferrous sulfate, $FeSO_4$, and ammonium sulfate, $(NH_4)_2SO_4$, an alum?

Common alum has many uses but, for most of these the cheaper aluminum sulfate is just as good. The alums have one advantage for certain special uses—they crystallize better than the simple sulfate and consequently are more readily purified by fractional crystallization. Either alum or the plain sulfate is added to city water supplies to aid in removing suspended matter and bacteria. If the water is soft, a little lime is added at the same time to insure precipitation of the gelatinous aluminum hydroxide. The bicarbonates of hard water serve as well as the lime:

$$Al_2(SO_4)_3 + 3\ Ca(HCO_3)_2 \longrightarrow 3\ CaSO_4 + 2\ Al(HCO_3)_3,$$
$$Al(HCO)_3 + 3\ H_2O \longrightarrow Al(OH)_3 + 3\ H_2CO_3.$$

In sizing paper to prevent the spread of ink it is the practice to mix an alkaline rosin soap in the pulp with aluminum sulfate. The resulting reaction yields free rosin throughout the paper where it is wanted. On passing through hot rolls the rosin melts throughout the paper.

A number of aluminum salts are used as mordants, substances which fix the dye to the fiber.

Dyeing.—Of the three leading classes of fabrics, cotton, silk, and wool, the silk and wool are the easiest to dye. This is because their fibers are protein material and more reactive chemically than the cellulose of cotton. Although a few thousand dyes are known, they may be grouped as follows:

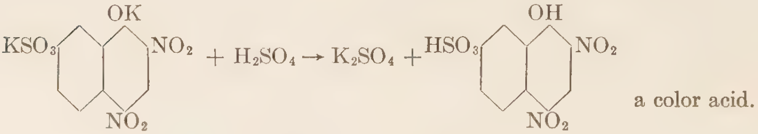
1. *The Indigo Type.* Solutions of dyes readily penetrate any fiber but wash out again unless the dye is held as an insoluble compound. For example, a fabric may be soaked in a solution of lead acetate and then in a solution of sodium chromate. Lead chromate is precipitated throughout the fabric and cannot be

washed out. Indigo is insoluble in water. To get it into the fabric in the first place it is necessary to reduce it by sodium hydrosulfite to the soluble, but colorless, indigo white. On exposing the fabric to the air this compound is oxidized to the insoluble blue indigo, now thoroughly entangled in every crevice and cell of the fibers.

2. ***Direct Dyes.*** Solutions of direct dyes diffuse into fabrics and either react with the fiber or are adsorbed powerfully on all surfaces. They are sometimes salted out by addition of sodium sulfate. Direct dyes for wool and silk are numerous, but for cotton they are relatively few.

The *acid dyes* are soluble salts of colored organic acids. When used in an acidified solution the dye acid is liberated and at once combines with the fiber to form a "color-lake." Such dyes act directly on animal fibers in presence of acid, due, no doubt, to the basic NH_2 groups of such protein fibers as wool and silk.

$$\text{Sodium salt of a color acid} + H_2SO_4 \rightarrow \text{color acid} + Na_2SO_4$$
$$\text{Color acid} + \text{protein fiber} \rightarrow \text{color-lake}$$



Potassium salt of a color acid

Dinitro-naphthol-sulfonic acid (Naphthol yellow S)

Every corner in the above structural formula is really occupied by a carbon atom to which is attached one hydrogen atom or the groups written above.

3. ***Mordant Dyes.*** There are many beautiful dyes not retained by cotton without help. This help is secured by the use of aluminum hydroxide. Now this hydroxide is insoluble and hence cannot be worked into the fibers. However, if a solution of aluminum acetate penetrates the material, its natural hydrolysis can be increased by boiling or a base may be added. By this device the insoluble aluminum hydroxide is formed throughout the fiber. A soluble dye penetrating below the surface is held by the hydroxide, so the dyed material becomes fast to washing. Other mordants are used, such as chromium hydroxide or even tannic acid. The latter material forms insoluble tannates with basic dyes. Mordant action can be demonstrated in a test tube. To a solution of alum and a dye add a base. Filter and wash the

precipitate. It retains the dye. Such compounds are called *lakes* and in dyeing they are formed in the fiber.

Two thousand years or more ago only royalty could wear Tyrian purple, a color developed when a fluid secreted in minute quantities by a snail-like shell-fish (*murex*) was exposed to sun and air. Yet this "royal purple" was not equal to the di-brom derivative of indigo now sold cheaply.

Indigo is the greatest dye used. It was formerly made from a plant grown in India, but about 1897 a method was developed for preparing it from naphthalene. The natural product was almost driven from the market. Alizarin, a famous red dye, was formerly made from madder root but it, too, has become a synthetic product. There are still some important natural dyes, such as logwood and fustic, in use, but most dyes are derived from coal tar. The American dye industry has grown tremendously because of the war's stimulating effect and now there are very few of the former imported dyes not yet equaled or excelled in this country. The manufacture of military explosives and the synthesis of dyes go hand in hand. They use the same raw materials to a marked extent and facilities for producing dyes are quickly adapted to the manufacture of explosives. Evidently our military preparedness in the future rests upon the existence of a prosperous dye industry.

The United States annual production of synthetic dyes is 100,000,000 pounds, much of which is exported. Imports of a few special dyes reach 6 per cent of our total needs. Such independence, largely attained since 1914, adds to the national safety, for from the nature of things, dye plants and dye chemists can quickly be set at work making munitions of war.

Brick and Pottery.—Kaolin or china clay is the weathered residue from rock feldspar. Its composition is represented by $H_2Al_2(SiO_4)_2 \cdot H_2O$, while that of feldspar is $KAlSi_3O_8$. Common clay owes its color to impurities, usually oxides of iron. In burning brick or tile the impurities fuse and act as a bond for the clay particles. Fire brick, with its great infusibility, must be made from rather pure clay.

Porcelain is a fired mixture of kaolin and feldspar. The more fusible feldspar binds the kaolin particles and makes the mass translucent. When such ware is dipped into a water suspension of ground feldspar, dried and burned again, it receives a glaze of feldspar. Cheaper ware may be so porous that a glaze is absolutely essential, as in ordinary table dishes. If the glaze has a different coefficient of expansion from the body of the ware, it cracks with temperature changes.

Portland Cement.—The Romans ground together volcanic ashes and lime with formation of a cement that, when mixed with water, set to a solid. Some specimens of this Puzzolan cement are still in good condition. To-day we do practically the same thing in grinding together blast furnace slag (granulated) and lime. But the best of these hydraulic cements is the modern Portland cement. The essential raw materials are clay and limestone. There must be present the proper equivalents in combined form of CaO, SiO_2 and Al_2O_3. The average composition of Portland cement is about as follows:

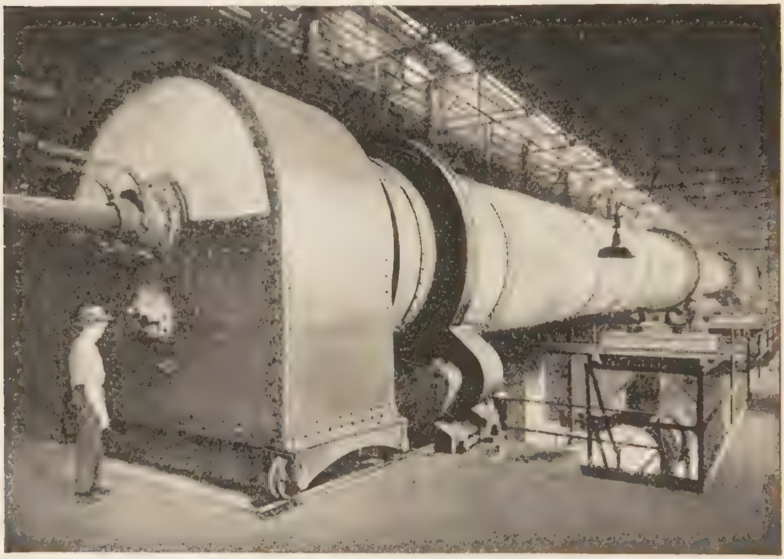


FIG. 154.—A rotary Portland cement kiln, 190 feet long. It is fired with a flame of powdered coal.

CaO	63 per cent	Fe_2O_3	2.5 per cent
Al_2O_3	6.5 " "	MgO	2.5 " "
SiO_2	21.5 " "	SO_3	1.5 " "

In the Rosendale district of New York and elsewhere there are cement rocks which approximate this composition, but usually clay and limestone are used. The raw materials are finely ground, fired in a rotary kiln to incipient fusion (the edges of lumps just melting), and the clinkered product ground again. These rotary kilns are nearly horizontal, from 60 to 200 feet long and 6 to 9 feet in diameter (Fig. 154). They are heated with powdered coal (see copper smelting). Nearly 8,000,000 tons of powdered coal are used as fuel in the cement industry, annually.

The materials enter at the cooler end of the kiln, slowly working down to the end where the flame enters. The product is a calcium aluminate and calcium silicate. About 3 per cent of gypsum ($CaSO_4$) is added to retard setting. A little iron oxide and magnesium oxide are allowed, but there is a definite range of concentrations for all the constituents. The cement powder when used for walls, walks, etc., is mixed wet with sand and gravel as a filler to form *concrete*. One part of cement is added to 4 parts sand and 8 of gravel. The surfacing mixture contains one part cement to 2 or 3 of sand. In 1928 the United States produced 176,000,000 barrels.

Common hydraulic cement is probably a mixture of calcium silicate, calcium aluminate and an excess of lime. Consequently it is highly basic. Hardening is due to hydration, hydrolysis and crystallization.

$$Ca_3(AlO_3)_2 + 6\ H_2O \longrightarrow 3\ Ca(OH)_2 + 2\ Al(OH)_3.$$

The calcium hydroxide formed as in the above equation slowly crystallizes and cements together the particles of calcium silicate. The aluminum hydroxide fills in.

Alumina Cements.—France has developed, of late years, a quick-setting cement, high in alumina ("ciment fondu"). The following comparison of composition for this and the ordinary Portland cement is interesting:

	PORTLAND CEMENT	ALUMINA CEMENT
Silica	23	10
Alumina	7	42
Lime	64	42
Iron	4	6
Miscellaneous	2	—
	100 per cent	100 per cent

After complete fusion (1400° C.) of the raw materials in the electric furnace, the mass is cooled and ground fine. With this hydraulic cement repairs may be made on roads and streets upon which traffic is so heavy that interruption is extremely serious. Roads so repaired have been safely used after 24 hours instead of several days, as with Portland cement repairs.

EXERCISES

2. What light metals may compete with aluminum?

3. What are the chief aluminum alloys?

4. What is an alum? Name some.

5. Define a double salt; a complex salt. Name some complex mercury salts.

6. How is Portland cement made and used?

7. How much aluminum may be obtained from 1 metric ton (1000 Kg.) of an ore, which is 85 per cent bauxite $Al_2O_3 \cdot 2\ H_2O$?

8. A certain sample of bauxite contained 12 per cent iron oxide and 88 per cent $Al_2O_3 \cdot 3\ H_2O$. How many grams of the ore would be required to produce 1000 g. of aluminum?

9. What weight of aluminum oxide can be obtained from 100 g. of sodium aluminate ($NaAlO_2$)?

10. What weights of sodium, zinc, and aluminum, respectively, would release 120 cc. of hydrogen (standard conditions) from hydrochloric acid?

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CHAPTER XLIV

TIN AND LEAD

TIN

Occurrence.—Tin ores are so easily smelted that the metal was known to the ancients. It was brought by the Phœnicians to Egypt and to Greece from the "Islands of the Cassiterides" now known as the British Isles. The tin mines of Cornwall have been, up to recent times, the chief source of this metal. At present most of it comes from the East Indies, and Bolivia, although China, and Nigeria are large producers. The chief ore, almost the only ore, is the crude dioxide, SnO_2, called cassiterite or tin stone.

Metallurgy.—All tin ores are concentrated by washing away the gangue and are then roasted in long rotary kilns like Portland cement kilns. By this process sulfur is oxidized to the dioxide. Arsenic is oxidized to the trioxide, which is collected in a cooling chamber—later to be sold as a valuable by-product. After this preliminary roasting the tin oxide is heated with carbon in a furnace, where it is reduced to the metal. In order to separate the tin from the bismuth, zinc, copper, and iron, which are usually present in it, advantage is taken of the surprisingly low melting point of the pure metal, 232°. The foreign metals are present as higher melting tin alloys. The mass is heated hot enough to melt pure tin, but not hot enough to melt the alloys. The pure liquid tin is poured off. This process of "liquation" is repeated many times while the dross is thrown back to be reduced. By another process the reduced ore is melted in a small reverberatory furnace. This produces a slag containing most of the impurities, and a metal, which is cast into anodes for electrolytic refining.

In 1928 the world produced 160,000 tons of tin, the United States using over half of this amount. There is but little prospect of an increase in production although demand grows steadily. Substitutes must be found.

Properties.—Tin is a white metal melting at 232° and boiling at 2275°. Its density averages 7.3. Below 18° tin tends to change into a gray powder with increase in volume. This change is most rapid at about −48° and when the metal is in contact with some of the gray modification. This "tin disease" was first observed when some organ pipes in the northern part of Russia during prolonged cold weather crumbled to dust. At another time, block tin stored in the old Russian capital developed this disease. It must be admitted that this change is rare, but if held at very low temperatures and inoculated with the gray powder all ordinary tetragonal tin would change. Tin is most malleable at 100°, while at 200° it is so brittle that it can be ground to a powder. (What other metals become brittle when heated?) Tin is plated on thin sheets of iron or steel by mere dipping of the clean steel into melted tin. The sheet must first be carefully pickled to free it from all oxides of iron. The modern ideal in tin-plating is to secure as thin a coating of tin as possible, without holes or cracks. From such tinned sheets are made common tin cups, pails, pans, and a hundred cheap and useful articles. Our dependence upon tin will become evident to all if this country is ever blockaded for a considerable period, as was Germany. Then the canned-food industry will have to rely upon glass; soldering of metal joints will be impossible; and substitutes for a great number of common tin utensils will have to be prepared. Tin is essential in soft solder and in bronze.

Chemically, tin is not very active. It is affected neither by the moisture nor by the carbonic acid of air and is therefore slowly tarnished. It is this property that makes it so useful. In acids the metal dissolves slowly. Dilute nitric converts it into stannous nitrate, $Sn(NO_3)_2$, with evolution of hydrogen. Rather concentrated nitric acid converts tin into an insoluble oxide, SnO_2. Dry chlorine attacks the metal much more readily than it does iron, so tin scrap is treated with chlorine. Anhydrous stannic chloride, $SnCl_4$, is secured. Hot concentrated sulfuric acid converts tin into stannic sulfate, $Sn(SO_4)_2$.

Iron is between zinc and tin in activity, so it is interesting to compare the wearing qualities of galvanized iron and tinned iron. Since zinc is more active than iron, it is the first to go when a crack or puncture exposes both metals to the attack of moisture and carbon dioxide. In such a galvanic couple the more active element dissolves first. Not so with tin. A puncture or crack means the rapid loss of iron, more rapid than if the tin coating had never been there. Of these two the iron is the more active. So tin plate is excellent until the iron is exposed, and then it is worse than no plate.

STANNOUS COMPOUNDS

When tin is dissolved in acids the hydrogen evolved insures the formation of salts of the lower valence. The same is true of iron and other metals, which exhibit two valences. If any stannic chloride were formed, it would be reduced by the nascent hydrogen:

$$\mathrm{Sn} + 2\,\mathrm{HCl} \longrightarrow \mathrm{SnCl_2} + \mathrm{H_2},$$
$$\mathrm{SnCl_4} + 2\,\mathrm{H} \longrightarrow \mathrm{SnCl_2} + 2\,\mathrm{HCl}.$$

Stannous Oxide and Hydroxide.—Stannous chloride reacts with a solution of sodium hydroxide to form the white, gelatinous hydroxide, $Sn(OH)_2$. The oxide, SnO, is a black powder precipitated by adding warm stannous chloride to a solution of sodium carbonate. When dry it can be burned in the air. Stannous hydroxide is much like zinc hydroxide and aluminum hydroxide in that it ~~dissolves~~ in strong acids as well as in strong bases. Therefore it is amphoteric.

$$\mathrm{Sn}\Big\langle\boxed{\begin{array}{c}\mathrm{OH + H}\\ \hline \mathrm{OH + H}\end{array}}\begin{array}{l}\mathrm{Cl}\\ \\ \mathrm{Cl}\end{array} \longrightarrow \mathrm{Sn}\Big\langle\begin{array}{l}\mathrm{Cl}\\ \\ \mathrm{Cl}\end{array} + 2\,\mathrm{H_2O},$$

$$\mathrm{Sn}\Big\langle\begin{array}{l}\mathrm{O}\\ \\ \mathrm{O}\end{array}\boxed{\begin{array}{lcr}\mathrm{H} & & \mathrm{HO}\\ \text{—} & + & \text{—}\\ \mathrm{H} & & \mathrm{HO}\end{array}}\begin{array}{l}\mathrm{Na}\\ \\ \mathrm{Na}\end{array} \longrightarrow \mathrm{Sn}\Big\langle\begin{array}{l}\mathrm{ONa}\\ \\ \mathrm{ONa}\end{array} + 2\,\mathrm{H_2O}.$$

The soluble salt, $Sn(ONa)_2$, is called sodium stannite, which suggests that stannous hydroxide may also be termed *stannous* acid.

Stannous Chloride, $SnCl_2$.—A solution of this salt is prepared by dissolving tin in hydrochloric acid. The anhydrous salt, however, is made by passing hydrogen chloride over hot tin. The solutions are acid by hydrolysis. "Tin salt," used as a mordant in dyeing, is $SnCl_2 \cdot 2\,H_2O$. Its solution is a good reducing agent. For example it reduces mercuric chloride to metallic mercury:

$$(1)\quad \mathrm{SnCl_2} + 2\,\mathrm{HgCl_2} \longrightarrow 2\,\mathrm{HgCl} + \mathrm{SnCl_4},$$
$$(2)\quad \mathrm{SnCl_2} + 2\,\mathrm{HgCl} \longrightarrow 2\,\mathrm{Hg} + \mathrm{SnCl_4}.$$

Stannous Sulfide, SnS.—This insoluble brown-black sulfide is precipitated by hydrogen sulfide from solutions of stannous salts:

$$\mathrm{SnCl_2 + H_2S \longrightarrow SnS + 2\,HCl.}$$

As this reaction shows, it is not dissolved by dilute acids. However, it is soluble in concentrated hydrochloric acid. Unlike the lower sulfides or arsenic and antimony, it is not soluble in the simple alkali sulfides. With polysulfides it forms the soluble sulfostannates so important in qualitative analysis:

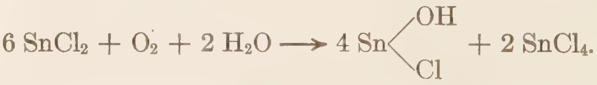
$$\mathrm{SnS + Na_2S_2 \longrightarrow Na_2SnS_3.}$$

On boiling some time with sodium sulfide, Na_2S, some stannic sulfide, SnS_2, is formed, and this reacts with the sodium sulfide to form the same product as above:

$$\mathrm{SnS_2 + Na_2S \longrightarrow Na_2SnS_3.}$$

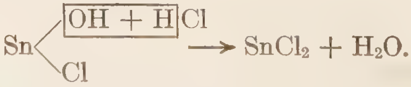
STANNIC COMPOUNDS

A solution of stannous chloride is partially oxidized in air with formation of stannic chloride and the basic chloride of stannous tin:



$$\mathrm{6\,SnCl_2 + O_2 + 2\,H_2O \longrightarrow 4\,Sn}\begin{matrix}\mathrm{OH}\\ \mathrm{Cl}\end{matrix}\mathrm{ + 2\,SnCl_4.}$$

By addition of acid this basic chloride is converted into stannous chloride:



$$\mathrm{Sn}\begin{matrix}\boxed{\mathrm{OH + H}}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\mathrm{\longrightarrow SnCl_2 + H_2O.}$$

The only way to keep a solution of a stannous salt is to have a few pieces of metallic tin and some acid present. The metal acts as a reducing agent, as does the hydrogen released.

Stannic compounds are not easily obtained from the dioxide, SnO_2, because this oxide is attacked with difficulty by acids. They are obtained indirectly from metallic tin or from stannous compounds.

Stannic Chloride, SnCl₄.—Stannic chloride is prepared in solution by passing chlorine into a solution of stannous chloride:

$$\mathrm{SnCl_2 + Cl_2 \longrightarrow SnCl_4.}$$

The anhydrous form is made by passing chlorine over hot tin. (See recovery from tin scrap.) It is a colorless liquid, fuming in moist air and boiling at 114°. It is a good solvent for sulfur, iodine, and phosphorus. With a little water it forms solid hydrates such as $SnCl_4 \cdot 5\ H_2O$, "oxymuriate of tin," which is used as a mordant in dyeing. On addition of more water, these hydrates dissolve. The solution slowly becomes turbid on boiling with precipitation of part of the stannic hydroxide formed. The rest remains in colloidal suspension.

Exercise 1.—If you added bromine water to a solution of stannous chloride, how would you know when all the tin was oxidized? Write the equation.

α-Stannic Acid, H_2SnO_3.—The alpha form of stannic acid is readily prepared by addition of ammonium hydroxide or sodium hydroxide to a solution of a stannic salt. We might expect $Sn(OH)_4$, but this loses water and yields H_2SnO_3. The rest of the water may be driven off and the anhydride, SnO_2, secured. The white gelatinous precipitate of α-stannic acid dissolves readily in excess alkali, forming stannates, such as Na_2SnO_3. The acid also dissolves easily in dilute mineral acids.

β-Stannic Acid, $(H_2SnO_3)_5$ (Metastannic acid).—When slightly diluted nitric acid reacts with tin, a hydrated form of the dioxide is produced as a white, insoluble powder. This form of stannic acid, unlike the alpha, is almost insoluble in dilute mineral acids. It is not readily attacked by alkalies, but if fused with sodium hydroxide it is converted into sodium α-stannate, identical with the salt secured by using the simple dioxide.

Tests.—Tin compounds are usually recognized by converting them into stannous chloride which reduces mercuric chloride to white, insoluble mercurous chloride and black finely divided mercury. The brown-black stannous sulfide, soluble in polysulfides, and the yellow stannic sulfide, soluble in alkali sulfides, are both well known in analysis. The ease of reduction of the oxide by hot carbon is noteworthy.

Lead

Occurrence.—Like tin, lead was known to the ancient Egyptians because of the ease with which its ores were smelted. The Romans used lead pipes for water service. The sulfide, PbS, or galena, is the most important ore, although cerussite, $PbCO_3$, anglesite, $PbSO_4$, and crocoite, $PbCrO_4$, are found. Lead ores are common all over the world. In 1928 the United States produced 627,300 tons and imported nearly two-thirds as much more.

Mexico, Australia, and Spain produced smaller amounts. Our chief lead district is in Missouri. Other fields are in Idaho, Utah, and Colorado.

Metallurgy.—The older reverberatory smelter has been displaced by the blast furnace. Part of the lead sulfide is first roasted to convert it into the oxide. This is then mixed with the raw ore, coke, and limestone, and added to the blast furnace, where it meets a strong blast of air. The burning carbon and the carbon monoxide formed are both good reducing agents, as we shall learn in connection with the smelting of iron ores. Lead oxide is reduced to the metal:

$$\begin{aligned} &(1)\quad 2\,PbS + 3\,O_2 \longrightarrow 2\,PbO + 2\,SO_2, \\ &(2)\quad 2\,PbO + C \longrightarrow 2\,Pb + CO_2, \\ &(3)\quad PbO + CO \longrightarrow Pb + CO_2. \end{aligned}$$

The iron present as an impurity is burned to the oxide and, as we shall also learn in the study of the iron blast furnace, it is reduced by hot carbon monoxide to the metal. But iron can extract sulfur from lead sulfide, so in this case an impurity is a genuine aid:

$$\begin{aligned} &(4)\quad Fe_2O_3 + 3\,CO \longrightarrow 2\,Fe + 3\,CO_2, \\ &(5)\quad PbS + Fe \longrightarrow Pb + FeS. \end{aligned}$$

The limestone carries off silica in the fusible slag, calcium silicate. A molten "matte" of iron sulfide with copper sulfide and some lead sulfide is separated for further extraction of lead.

Refining of lead usually involves the separation of antimony, arsenic, bismuth, and copper by oxidation. The lead is kept molten with stirring. These impurities oxidize more readily than lead and float to the surface as dross. Any gold or silver may be removed by Parkes' process (see silver) or by Betts' electrolytic process. Crude lead slabs are hung as anodes and thin sheets of pure lead as cathodes in a bath of aqueous hydrofluosilicic acid (H_2SiF_6) containing lead silicofluoride and 0.01 per cent gelatin (to insure coherence of deposit). With electrolysis the impurities drop as anode mud (compare with purification of copper). If antimony, arsenic, and copper were not removed, the lead would be hard and this would greatly cripple the usefulness of the element. We want some metals to be extremely hard and others to be extremely soft.

Properties.—Lead is a heavy metal of specific gravity 11.4, soft and easily cut with a knife. The metal melts at 327° and boils at 1525°. Just below its melting point it can be squeezed into tubes. When freshly cut, its luster is bright, but the surface quickly tarnishes with formation of oxide and basic carbonate. This coating protects the metal from further oxidation, although it detracts sadly from the real beauty of lead. A strip of zinc hung in a very dilute solution of a lead salt (acetate or nitrate) is soon covered with a "lead tree" of beautiful gleaming crystals of metallic lead:

$$Pb^{++} + Zn + NO_3^- + NO_3^- \longrightarrow Zn^{++} + Pb + NO_3^- + NO_3^-.$$

Chemically lead does not always seem as active as it really is. For example, cold hydrochloric acid scarcely attacks it. Lead chloride forms a protective coating over the lead. Hot acid dissolves this and permits the metal to be attacked. Lead sulfate, too, is insoluble and has a protecting action. But when above 80 per cent in concentration, sulfuric acid dissolves lead sulfate and consumes the metal. Nitric acid dissolves lead with release of oxides of nitrogen rather than of hydrogen. Acetic acid slowly attacks lead in the air, due to the preliminary oxidation of the metal. This reaction is fundamental in the manufacture of white lead paints.

Solutions of lead salts are extremely poisonous, so that water conducted through lead pipes may produce lead poisoning. This is particularly true of soft water, which with air forms $Pb(OH)_2$, somewhat soluble. Hard water is much less dangerous because it soon forms a coating of insoluble carbonate and sulfate on the lead. Therefore, a bright lead pipe is under suspicion. The worst feature of lead poisoning is that it is cumulative. Traces of lead may be taken into the body for years, but they remain. Painters and workers in lead industries have to be careful not to convey lead compounds to the mouth through any lack of care in washing the hands.

Exercise 2.—Why are we able to make sulfuric acid in lead chambers without loss of lead?

Lead is the cheapest metal after iron. Its resistance to the attack of moist air and of several acids makes it useful in lining vats or tanks. Sulfuric acid plants are lined with it, water pipes

$H_2SO_4 + PbSO_4 \rightarrow$

$HNO_3 + PbSO_4 \rightarrow$

are made of it (by forcing cold lead through holes under a pressure of 33 tons per square inch) and common shot formed from it. Solder is an alloy of lead and tin; Babbitt (antifriction bearing metal) is a lead alloy; type metal contains it; and the collapsible metal tube containers for pastes are lead alloys. Storage batteries use lead plates and all lead paints begin with lead as raw material. It is the standard cable covering.

- Lead
  - Bearing metals
  - Type metal
  - Storage battery plates
  - Solders
  - Expansion bolts attaching iron to stone
  - Toys
  - Electric fuses
  - Collapsible tubes
  - Lead pipe
  - Sheet lead
  - Cable covering
- Lead Compounds
  - Paint Industry
    - White lead
    - Red lead
    - Orange mineral
    - Chrome yellow
    - Basic lead sulfates
  - Glass, Pottery Industry
    - White lead
    - Red lead
    - Litharge
  - Rubber Industry
    - White lead
    - Basic lead sulfate
    - Litharge
  - Match Industry
    - Red lead
    - Lead peroxide
  - Storage Battery Industry
    - Red lead
    - Litharge
  - Linoleum Industry
    - Same compounds as in Paint Industry
  - Textile Industry
    - Lead nitrate
    - Lead acetate
    - Litharge
  - Medicine
    - Lead acetate
  - Insecticides
    - Lead arsenate

Recently lead mattresses have come into use as shock absorbers for skyscrapers resting on rock foundations.

Oxides.—There are five oxides of lead, although only two are in common use:

Pb_2O, lead suboxide, gray,
PbO, lead monoxide (litharge), yellow-red, Base
Pb_2O_3, lead trioxide, orange yellow,
PbO_2, lead dioxide or peroxide, chocolate brown, Base
Pb_3O_4, lead tetroxide (minium or red lead), red. Base

Lead Monoxide (Litharge), PbO.—This yellow-red powder is obtained by heating lead in the air. It would probably be yellow, but for the presence of more or less red lead, Pb_3O_4, also formed by heating lead in air. Above 600° all lead oxides pass into the monoxide. It is used in glazing pottery, making glass (of the cut-glass type) and is a starting point in preparing other lead compounds.

Lead oxide is the anhydride of $Pb(OH)_2$, sometimes called plumbous hydroxide, and sometimes plumbous acid. It is precipitated by the union of Pb^{++} ions and OH^- ions. With acids and alkalies it reacts like zinc hydroxide, yielding soluble lead salts or soluble plumbites:

Pb_2O_3

$$\mathrm{Pb}\begin{cases}\boxed{\mathrm{OH + H}}\,\mathrm{NO_3}\\ \boxed{\mathrm{OH + H}}\,\mathrm{NO_3}\end{cases} \qquad \mathrm{Pb}\begin{cases}\mathrm{NO_3}\\ \mathrm{NO_3}\end{cases} + 2\,\mathrm{H_2O},$$

$$\mathrm{Pb}\begin{cases}\mathrm{O}\boxed{\mathrm{H} + \mathrm{HO}}\,\mathrm{Na}\\ \mathrm{O}\boxed{\mathrm{H} + \mathrm{HO}}\,\mathrm{Na}\end{cases} \qquad \mathrm{Pb}\begin{cases}\mathrm{ONa}\\ \mathrm{ONa}\end{cases} + 2\,\mathrm{H_2O}.$$

Exercise 3.—How does the existence of lead carbonate in water suspension show that $Pb(OH)_2$ is not an extremely weak base?

Lead Dioxide, PbO₂.—The simplest method of preparation is to add bleaching powder to a solution of sodium plumbite:

$$\mathrm{Ca(OCl)Cl + Na_2PbO_2 + H_2O \longrightarrow PbO_2 + CaCl_2 + 2\,NaOH.}$$

The chocolate-brown powder is a powerful oxidizing agent. Hydrogen sulfide gas passed over it is ignited. It may be considered the anhydride of plumbic acid (or hydroxide), $Pb(OH)_4$.

Red Lead, Pb₃O₄.—Red lead, or minium, is prepared (40,000 tons annually in the United States) by carefully heating litharge,

PbO, in air not above 545°. Above that temperature it decomposes into the monoxide and oxygen.

$$\underset{\text{(at 545°)}}{6\ PbO + O_2} \rightleftarrows \underset{\text{(above 545°)}}{2\ Pb_3O_4.}$$

It is used in considerable quantities as a pigment in red paints and also as an oxidizing agent.

The Halides of Lead.—Lead chloride, $PbCl_2$, formed by the union of Pb^{++} ions and Cl^- ions or by the action of hot concentrated hydrochloric acid on the monoxide or carbonate, is somewhat soluble in hot water, but only sparingly soluble at room temperatures. On cooling the hot water solution white crystals separate. It is much more spectacular to cool a hot water solution of the yellow lead iodide, PbI_2. Beautiful gleaming gold crystals settle like so many spangles. The bromide is much like the chloride and iodide in solubility. All these halides of lead form complex salts with the alkali halides (compare with mercuric halides).

Fig. 155.—Grinding oil into a lead paint.

White Lead.—A paint is prepared by grinding some heavy insoluble *pigment* of sufficient covering power with linseed oil. The drying of paint is not really a loss of water, but oxidation of the oil with formation of a tough, solid film. This oxidation of the oil is hastened by catalytic dryers made by boiling manganese dioxide, etc., with linseed oil. Among the pigments used are white lead, red lead, barium sulfate, lead chromate, zinc oxide, lithopone, iron oxides, and others, but the one most used is ***white lead*** or basic lead carbonate, $Pb(OH)_2 \cdot 2\,PbCO_3$. In the United States alone nearly 200,000 tons are used annually.

By the famous ***"Old Dutch"*** process, lead sheets rolled into "buckles" are placed in earthenware pots just above some dilute acetic acid. A layer of these pots is set on spent tan bark from the tannery, another layer of pots is supported by loose boards above the first, then a layer of tan bark and so on until a chamber 20 x 20 x 30 feet is filled. Fermentation of the tan bark yields carbon dioxide and heat, up to 85° C. The heat vaporizes acetic acid and moisture, which attack the lead with the formation of basic lead acetate. The carbon dioxide changes this into basic lead carbonate. After three or four months the sealed chamber is opened. The corroded buckles are rolled to flatten fragments of lead, which are finally washed and screened through silk cloth containing 30,000 openings to the square inch. The fine white powder is ground in oil and marketed.

The Lead Storage Battery.—A charged lead storage cell consists of a lead plate surfaced with lead dioxide as the positive pole and a second lead plate surfaced with spongy lead as the negative pole—both immersed in 20 per cent sulfuric acid.

When the two poles are connected by a metallic circuit some of the lead atoms on the surface of the lead plate give up electrons to the rest of the plate (making the plate negative) and go into solution as Pb^{++} ions. They do not go far, however, for they meet SO_4^{--} ions in the solution and are deposited on the plate as insoluble $PbSO_4$.

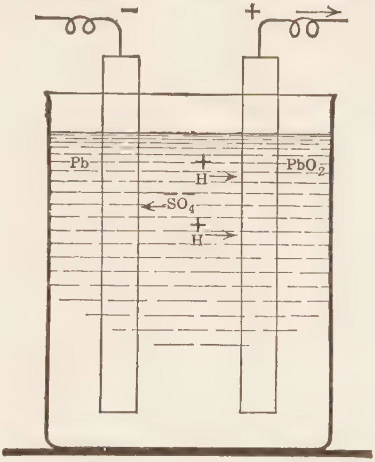


FIG. 156.—A charged cell.

The two electrons given to the lead plate, when Pb^{++} ions are formed, travel along the metallic conductor to the brown lead peroxide plate, PbO_2. There they unite with H^+ ions of the solution which on discharge promptly reduce the PbO_2 to PbO, a basic oxide that readily reacts with sulfuric acid to form $PbSO_4$.

Discharge

$$\begin{aligned}
&(1)\quad PbO_2 + 2\,H^+ + 2(-) \longrightarrow PbO + H_2O\\
&\qquad\qquad PbO + H_2SO_4 \longrightarrow PbSO_4 + H_2O,\\
&(2)\qquad\qquad Pb + SO_4^{--} \longrightarrow PbSO_4 + 2(-).
\end{aligned}$$

On passing a current through the exhausted cell (as in electroplating) sulfuric acid is electrolyzed, its H^+ ions discharged on the $PbSO_4$ surface of the lead electrode reducing the lead sulfate again to the original sponge lead and forming more H_2SO_4. At the other electrode (brown PbO_2 now surfaced with $PbSO_4$) the current discharges SO_4^{--} ions which then unite with the $PbSO_4$ to form $Pb(SO_4)_2$, lead disulfate. This, however, is easily hydrolyzed to the original brown PbO_2, lead dioxide, and to H_2SO_4.

Charge

$$\begin{aligned}
&(3)\quad PbSO_4 + 2\,H^+ + 2(-) \longrightarrow Pb + H_2SO_4\\
&\qquad\qquad PbSO_4 + SO_4^{--} \longrightarrow Pb(SO_4)_2 + 2(-),\\
&(4)\qquad Pb(SO_4)_2 + 2\,H_2O \longrightarrow PbO_2 + 2\,H_2SO_4.
\end{aligned}$$

The action in charging is just the opposite of that in discharging. It is chemical energy that is stored up, not electrical. If lead sulfate were formed by other means than the discharge of a storage cell, much heat would be released. With this battery nearly all that energy is converted into electricity. In practice it is unwise to convert too thick a layer of the plates into lead sulfate, for regeneration becomes difficult, possibly due to a lack of permeability. Nor should a discharged cell stand long before charging. Otherwise the lead sulfate coating becomes more compact. The normal voltage of such a cell, fully charged, is about two volts, but this falls on discharge. Thus there are two ways of learning the condition of the cell: measuring the density of the acid and the potential fall between the poles. Since sulfuric acid is used

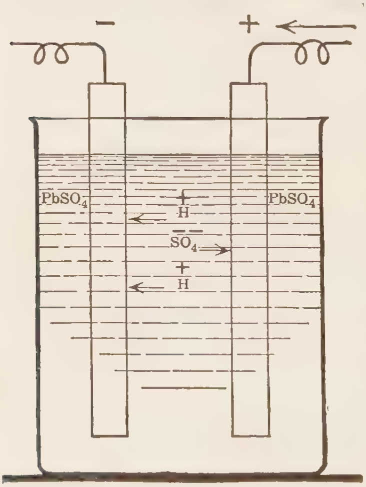


FIG. 157.—A discharged cell.

up on discharge, the density of the liquid falling to 1.10 and since sulfuric acid is reformed on charge with a rise in density to 1.30 it is a simple matter to learn the cell-condition.

The Edison Storage Cell.—It is interesting to compare the Edison cell with the lead cell. In the Edison type a 21 per cent solution of KOH is the electrolyte and the poles are iron and an oxide of nickel.

$$\underset{\rightarrow \text{Discharge}}{Ni_2O_3 + Fe + 3\,H_2O} \rightleftarrows \underset{\leftarrow \text{Charge}}{2\,Ni(OH)_2 + Fe(OH)_2}.$$

Storage cells are used in submarines, in small isolated lighting plants, for ignition in gasoline engines, for self-starters in autos, and for many other purposes where direct current is needed.

The Tin-Lead Group

Other elements in this group are titanium, zirconium, thorium, and germanium (predicted by Mendeleef).

Hafnium

Hafnium was announced as a new element in January, 1920, by Coster and Hevesy of the University of Copenhagen. They discovered it, by the aid of X-ray spectra, in several zirconium minerals. In fact its properties resemble those of zirconium. So far it has not been separated in pure form.

EXERCISES

4. When tin is treated with hydrochloric acid what is formed? When tin is treated with concentrated nitric acid what is formed?
5. How is litharge made? Red lead? "White lead"?
6. How does a lead storage battery operate on charge and on discharge?
7. How many grams of lead sulfate are formed when 150 g. of lead are converted first into lead acetate then into the sulfate (95% yield)?
8. How many grams of lead are there in 73 g. of pure litharge? How many grams of tin in 73 g. of pure stannic oxide?
9. Calculate the percentage composition of the two chlorides of tin and show that they illustrate the law of multiple proportions.

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CHAPTER XLV

CHROMIUM AND MANGANESE

Although chromium is found in the seventh group of the periodic table and manganese in the eighth, they have so many points in common that they should be studied together. Moreover, chromium has no great resemblance to the other members of its subgroup. These two elements are remarkable for the number of their oxidation stages and the great variety of their compounds. Their lower oxides are basic and their higher oxides acidic (compare with lead).

CHROMIUM

Occurrence.—Vauquelin first prepared the metal (1797) by making chromium oxide from the mineral crocoite, $PbCrO_4$, and reducing this oxide with carbon. The only important ore for commercial purposes is chromite, $Fe(CrO_2)_2$, sometimes written $FeO \cdot Cr_2O_3$ which has already been mentioned as a spinel (see magnesium). It is mined in Rhodesia, India, Cuba, and New Caledonia (near Australia). California produced heavily in the war emergency. For fifty years after 1827 the chromite deposit of Maryland-Pennsylvania supplied the world, largely for the manufacture of colors. In 1869 chrome-steel manufacture was initiated by an American company. We import yearly 250,000 tons. A large deposit has recently been found near Yellowstone Park.

Metallurgy and Properties.—Until the recent development of chrome plating the free element was not prepared in great quantity, as its alloy with iron is cheaper and more suitable for steel making. Most of this alloy, "ferrochrome," is made by carbon reduction of chromite in the electric furnace. A small amount of the carbon-free alloy is made by the Goldschmidt process (p. 561). Ferrochrome, carrying 60 per cent of the metal, is added to special steels used for safes, armor plate, projectiles, autos, and high-speed tools.

It is difficult to overstate the importance of chromium among the metals. Alone it is of little importance but in the various alloys it is a key metal. Chromium in alloy steels increases hardness and strength without sacrificing toughness or ductility. Without such chromium steels the weight of the engine in a powerful automobile would make the car absurdly clumsy. Furthermore the airplane would be an impossibility. Nearly all the alloy steels contain 1 or 2 per cent of chromium. Even the high-speed cutting tools owe their merit to the combination of chromium and tungsten rather than to tungsten alone. "Rustless iron" contains 13 per cent chromium but only 0.10 per cent carbon, thus differing from "stainless steel" with a 0.4 per cent carbon and 13 per cent chromium content. This iron is coming into use for roofing.

"Nichrome," an alloy of chromium with nickel, is extensively used in the form of wire or ribbon as resistance material for electric heaters. It contains 60 per cent nickel, 14 per cent chromium, and 16 per cent iron.

Chromium is an important constituent of the white stainless alloy known as "stellite." When made of chromium and cobalt this alloy is used in making such articles as table knives and spoons. With a little added tungsten the alloy becomes harder than any steel and stands up under much higher speeds on the lathe than high-speed steel tools. Since it is hard and stainless stellite is suitable for pocket knives, surgical instruments, and the like.

Chromium is a brilliant, silvery metal, hard and brittle. It melts at 1520° and has a density of 6.9. The powdered metal burns in oxygen with formation of the trioxide, Cr_2O_3. With chlorine it forms the chloride, as it does with hydrochloric acid. In fact, it is easily attacked by cold concentrated or hot dilute hydrochloric and sulfuric acids. Yet nitric acid does not affect the metal.

Chromium is now attracting the attention of many manufacturers. The value of chromium as a metal in its own right lies in (1) its great hardness and hence its suitability for printing plates, dies, gages, cams and gears, (2) its high luster and resistance to tarnish, which render it useful for exposed reflectors, and (3) its resistance to atmospheric corrosion. These properties led the way to chromium plating, usually over nickel plating, on automobile radiator shells, bumper bars, plumbing fixtures and other objects. Chromium plating, usually from solutions containing chromic acid and soluble sulfates, is already in extensive use. Great care must be taken to avoid skin contact with the chromic acid spray or annoying ulcers result.

Series of Chromium Salts.—As illustrations of the different series to which salts of chromium belong there are presented such salts as

$$CrSO_4 \text{ and } CrCl_2,$$

chromous sulfate and chromous chloride. These salts are evidently derived from a basic oxide, CrO, in which the element chromium is bivalent.

There is a second series of salts, illustrated by

$$Cr_2(SO_4)_3 \text{ and } CrCl_3,$$

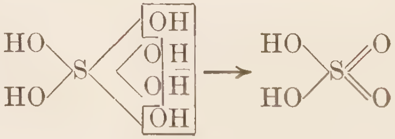
chromic sulfate and chromic chloride, derived from the basic oxide, Cr_2O_3, in which the valence of the element is three.

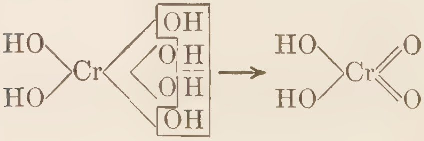
Exercise 1.—Write the equations showing how these four salts could be prepared by the action of the appropriate acids on oxides or hydroxides of chromium.

Quite different from the preceding are the salts of the series illustrated by

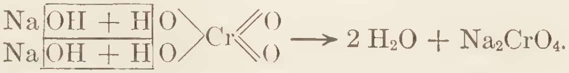
$$K_2CrO_4 \text{ and } Na_2CrO_4,$$

potassium chromate and sodium chromate. The oxide of chromium from which these salts are derived is represented by the formula CrO_3, in which chromium has a valence of six, like sulfur in sulfuric anhydride, SO_3. Like the latter also, this oxide of chromium acts as an acid anhydride and is known as "chromic anhydride." This particular oxide can be prepared in red crystals. It must be the anhydride of chromic acid, H_2CrO_4, just as SO_3 is the anhydride of sulfuric acid. Since the central element in each oxide has a valence of six, it is logical to consider the possible existence of acids in which all six valences are used to hold —OH groups. Such acids are unstable and by instant loss of water form the partly dehydrated products we work with in the laboratory, H_2SO_4 and H_2CrO_4:





The student must keep clearly in mind that the mere presence of OH groups does not guarantee the formation of OH^- ions in water solution. Nearly all acids contain OH groups, but it is only the hydrogen that is split off in ionic form. This acidic ionization is illustrated in the following equation:



$$\begin{matrix} \text{Na}\boxed{\text{OH} + \text{H}}\text{O} \\ \text{Na}\boxed{\text{OH} + \text{H}}\text{O} \end{matrix} > \text{Cr} \begin{matrix} \text{O} \\ \text{O} \end{matrix} \longrightarrow 2\,H_2O + Na_2CrO_4.$$

Lastly, there are such salts as:

$$K_2Cr_2O_7,$$

which may be written, $K_2O \cdot 2\,CrO_3$, somewhat like the salts of pyrosulfuric acid. The chromate, K_2CrO_4, could be written $K_2O \cdot CrO_3$. In $K_2Cr_2O_7$, the oxide of chromium is the same as in K_2CrO_4. Therefore, no new valence series is illustrated, but a new set of chromates, just as there are two sets of phosphates, ortho and meta, and two sets of sulfates derived from the ortho and pyro acids.

There are, therefore, three principal series of salts of chromium —chromous, chromic, and chromates. Of these, the chromous salts are so easily oxidized to the chromic forms that they are with difficulty preserved, and may be omitted from the list.

The normal electron arrangement in the chromium atom, counting electron shells from the nucleus out, is 2, 8, 8, 6 as in the chromates and dichromates. Here the valence shell contains six electrons. In the green and violet chromic salts the arrangement is 2, 8, 11, 3 and the valence shell contains only three electrons.

1. Chromous salts, derived from CrO; valence of chromium, 2.
2. Chromic salts, derived from Cr_2O_3; valence of chromium, 3.
3. Chromates, derived from CrO_3; valence of chromium, 6.

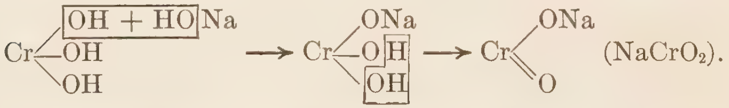
Chromous Compounds.—When chromium is dissolved in hydrochloric acid it is ***chromous chloride*** $CrCl_2$, not chromic chloride, $CrCl_3$, that is secured. The active hydrogen released and the excess metal would reduce any chromic chloride to the lower form. Since chromous salts are quickly oxidized by the air they are powerful reducing agents. ***Chromous hydroxide,*** $Cr(OH)_2$, is a yellow precipitate, while it lasts.

Chromic Compounds.—The insoluble anhydrous *chromic chloride,* $CrCl_3$, is prepared by the action of chlorine on chromium. The ordinary form and color of chromic chloride is soluble and green. It is easily made by reduction of a dichromate or of CrO_3 itself with alcohol in a solution of hydrochloric acid:

$$2\,CrO_3 + 6\,HCl + 3\,C_2H_5OH \rightarrow 2\,CrCl_3 + 3\,C_2H_4O + 6\,H_2O.$$

The aldehyde resulting from oxidation of the alcohol is volatile, so only the green solution of chromic chloride is left. Green chromic chloride may also be formed by the action of hydrochloric acid on chromic hydroxide.

Chromic Hydroxide, $Cr(OH)_3$.—This hydroxide is formed as a bluish-green amorphous precipitate when ammonium hydroxide is added to a solution of a chromic salt. The stronger bases could be used, but the hydroxide dissolves in an excess of sodium hydroxide. It is probable that the reaction proceeds as follows:



Chromic hydroxide also dissolves in acids, as it is amphoteric.

Chrome Alum, $KCr(SO_4)_2 \cdot 12\,H_2O$.—This double salt is formed by mixing solutions of potassium sulfate and chromic sulfate, $Cr_2(SO_4)_3$, in molecular proportions. From the resulting solution large and beautiful ruby crystals are secured on slow evaporation.

Green and Violet Chromic Salt Solutions.—All chromic salt solutions are green after boiling, but on standing in the cold they turn violet. The former change in color is accompanied by the disappearance of the simple Cr^{+++} ions. The violet color is believed to be due to Cr^{+++} ions and the green color to complex ions (p. 566).

Cold silver nitrate solution quickly precipitates all of the chlorine from a violet solution of chromic chloride but only a third of the chlorine from a green solution. Evidently in the green solution two of the three chlorine atoms in each molecule of $CrCl_3$ are not ionizable. A complex ion involving water molecules is formed.

$$\text{Green } Cr(H_2O)_4Cl_2 \cdot Cl \rightleftarrows Cr(H_2O)_4Cl_2^{+} + Cl^{-}.$$

Chromates and Dichromates.—The mineral chromite is the starting point in the manufacture of chromates. Fused in the air with potassium hydroxide or lime and sodium carbonate (possibly with addition of a solid oxidizing agent) chromite yields the *soluble* potassium chromate which on addition of acid is converted into the dichromate:

$$4\,Fe(CrO_2)_2 + 7\,O_2 + 16\,KOH \longrightarrow 2\,Fe_2O_3 + 8\,H_2O + 8\,K_2CrO_4.$$

Here the valence of chromium was raised from three to six. Addition of concentrated sulfuric acid to a solid chromate, or dichromate, liberates chromic acid, H_2CrO_4, or dichromic acid, $H_2Cr_2O_7$, and promptly dehydrates it into the anhydride, CrO_3. This precipitates in red crystals which readily dissolve in water and rehydrate to the acid.

Since potassium dichromate is much more soluble hot than cold, it is easily purified by crystallization. The remarkable change in color from the yellow chromate solutions to the orange-red dichromate solutions on acidifying, with the reverse action on neutralizing with a base, may be explained by supposing that the CrO_4^{--} ions react with H^+ ions to form $Cr_2O_7^{--}$ ions and water. Both chromate and dichromate solutions may exhibit the following equilibrium condition, shifted one way or another:

$$2\,CrO_4^{--} + 2\,H^+ \rightleftarrows Cr_2O_7^{--} + H_2O.$$

Addition of an acid increases the concentration of H ions and drives the reaction to the right. Addition of a base uses up the H^+ ions and drives the reaction to the left. Since both CrO_4^{--} and $Cr_2O_7^{--}$ ions are present in a dichromate solution, addition of Pb^{++} ions must result in formation of the more insoluble of the two salts, lead chromate and lead dichromate. Lead chromate is extremely insoluble and is precipitated. It is a yellow pigment used in paints. Barium chromate is a yellow precipitate formed under similar conditions. Sodium dichromate is used to the extent of 22,000 tons yearly in the "chrome tanning" of hides. It is reduced in the hide to the trioxide (Cr_2O_3), which forms an insoluble compound of some sort with the hide material.

The dichromates are used as commercial oxidizing agents. In oxidizing some substances the chromium falls in valence from six to three as illustrated here in reaction with sulfurous acid. Since the basic oxide, Cr_2O_3, is liberated in the reduction of a dichromate some extra acid is required to dissolve it as chromic sulfate.

$$K_2Cr_2O_7 + 3\ H_2SO_3 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4\ H_2O.$$

Tests.—Chromium compounds may be detected by conversion into chromic salts and by addition of sodium peroxide to a little of the very concentrated solution. The soluble yellow sodium chromate formed is slightly acidified and treated with a solution of a lead salt. Yellow lead chromate is precipitated.

$$\begin{aligned}
Na_2O_2 + H_2O &\longrightarrow 2\ NaOH + (O),\\
CrCl_3 + 3\ NaOH &\longrightarrow Cr(OH)_3 + 3\ NaCl,\\
Cr(OH)_3 + NaOH &\longrightarrow NaCrO_2 + 2\ H_2O,\\
2\ NaCrO_2 + (3\ O) &\longrightarrow Na_2Cr_2O_7,\\
Na_2Cr_2O_7 + 2\ NaOH &\longrightarrow 2\ Na_2CrO_4 + H_2O,\\
Na_2CrO_4 + Pb(NO_3)_2 &\longrightarrow 2\ NaNO_3 + PbCrO_4\ \text{(yellow)}.
\end{aligned}$$

When a chromate or dichromate is acidified and shaken with a solution of hydrogen peroxide, blue perchromic acid, $HCrO_4$, is formed. It is very unstable in this solution, but if a layer of ether is present the blue compound dissolves in the ether on shaking and lasts for some time. This reaction may be used as a test for chromium or for hydrogen peroxide. Chromium is grouped, in analysis, with ferric iron and aluminum because of the insolubility of its hydroxide. Like aluminum its hydroxide dissolves in excess base. Chromium compounds may also be detected if first converted into a soluble dichromate and then treated with a diphenyl carbazide reagent (diphenyl carbazide, Eastman, 0.2 g. in 10 cc. glacial acetic acid, diluted to 100 cc. with 95 per cent ethyl alcohol). The violet color results when chromium is present to the extent of one part in 100,000,000.

MANGANESE

Manganese is the only known member of its sub-group, but it is placed in the same column of the periodic table with the halogens. It resembles the halogen family very little, although Mn_2O_7 corresponds to Cl_2O_7 and $HMnO_4$ to $HClO_4$.

There are five series of manganese compounds, each with a different valence of the metal. With each valence manganese seems to belong to a different group of elements. The oxides from which the different series are derived are MnO, Mn_2O_3, MnO_2, MnO_3, and Mn_2O_7. All the stable oxides tend to give off oxygen and form manganous salts when treated with acid. If the acid is oxidizable, like hydrochloric, chlorine is released (except when MnO is used). Heated in the air with strong bases, these oxides tend to take up oxygen and yield derivatives of the two highest oxides.

Occurrence.—The chief manganese ore is pyrolusite, MnO_2, mined in India, Russia, South Africa and Brazil. Some manganese carbonate is mined in Montana. When our imports were partly cut off during the World War other manganese deposits were mined. There were extensive workings within the city limits of Butte, Montana, but with the coming of peace it no longer paid to work such inferior ores. We now import nearly 700,000 tons annually.

We must always depend upon importations for high-grade ores suitable for the manufacture of ferromanganese, but rather large and increasing amounts of low-grade ores are produced in the United States.

On some of the rich Florida soils addition of 50 pounds of manganese sulfate per acre gave a remarkable increase in crop yields. Of course this does not mean that all soils would profit by addition of manganese salts. Possibly some would be injured.

Metallurgy.—Manganese is rather difficult to prepare because, where the oxides are reduced with carbon in the electric furnace or blast furnace, some carbon unites with the metal. The pure element is prepared by Goldschmidt's method. Commercially the metal is of value mainly in the form of an alloy with iron. Such an alloy carrying less than 20 per cent manganese is called *spiegeleisen*, while an alloy carrying from 20 to 90 per cent is called ferromanganese. These alloys are added to steel to give it hardness and strength. A manganese steel carrying 11–14 per cent manganese, to mention an extreme case, is too hard to be machined and must be cast and ground to shape. Burglar-proof safes and armor plates are made of manganese steel.

Properties.—Manganese is a reddish-gray metal melting at 1260° and boiling at 1900°. It has been distilled in a high vacuum at a much lower temperature. It has a density of 7.2. It is very brittle and hard enough to scratch glass. In the air it is not tarnished, but acids as weak as acetic attack it, forming manganous salts.

Series of Manganese Salts.—The best way to compare the salts of manganese with those of chromium is to list the salt-producing oxides. These are:

1. Manganous salts (pink) derived from MnO; valence of Mn, 2. $MnSO_4$
2. Manganic salts (green) derived from Mn_2O_3; valence of Mn, 3. $Mn_2(SO_4)$
3. Manganates (green) derived from MnO_3; valence of Mn, 6. K_2MnO_4
4. Permanganates (purple) derived from Mn_2O_7; valence of Mn, 7. $KMnO_4$

The normal electron arrangement in the manganese atom should be 2, 8, 8, 7 and this is found in the permanganates. In the green manganates it is 2, 8, 9, 6 while in the manganic salts it is 2, 8, 12, 3. Finally, in the manganous compounds it is 2, 8, 13, 2 with only two valence electrons.

Illustrations of such salts are, in order, manganous sulfate, $MnSO_4$, manganic sulfate, $Mn_2(SO_4)_3$, potassium manganate, K_2MnO_4, and potassium permanganate, $KMnO_4$. Under chromium, the valences 3 and 6 were important, but with manganese compounds emphasis is placed on the valences 2 and 7.

Manganous Compounds.—Freshly precipitated manganous hydroxide, $Mn(OH)_2$, is of about the same order of solubility as magnesium hydroxide. Consequently ammonium salts dissolve it just as they dissolve the latter hydroxide. It is all a matter of decrease in OH^- ion concentration, due to the formation of weakly ionized ammonium hydroxide.

EXERCISE 2.—Review magnesium hydroxide and then write the equations for the solution of manganous hydroxide by ammonium salts.

Manganese sulfide is the most soluble sulfide of the heavy metals. It is not precipitated by hydrogen sulfide unless a base or considerable sodium acetate be added. In the usual system of qualitative analysis, this pink sulfide is precipitated by ammonium sulfide. It oxidizes so readily in the air to the soluble manganous sulfate, $MnSO_4$, that analysts are accustomed to wash it with hydrogen sulfide water.

Manganese Dioxide, MnO_2.—Manganese tetrahydroxide, $Mn(OH)_4$, a very weak acid, readily breaks down into water and manganese dioxide. This oxide is by far the most important compound of manganese. The mineral form is used in dry batteries as a depolarizer. Glass was once decolorized by addition of manganese dioxide. Ferromanganese is made from the dioxide, which is also used to make dryers for paints. It is so very weak a base or acid that it is almost in a class by itself. Yet with cold concentrated hydrochloric acid it forms manganese tetrachloride, $MnCl_4$. On warming this gives off chlorine. (Equations?) On dilution it is hydrolyzed like lead tetrachloride, $PbCl_4$, to the dioxide. (Diagram this action.)

Transformation in the Manganese Series

All the stable oxides tend to give off oxygen and form manganous salts when treated with acid. If the acid is oxidizable, as hydrochloric, chlorine is released (except where MnO is used). Thus such salts as manganous chloride, $MnCl_2$, and manganous sulfate, $MnSO_4$, are formed:

$$\begin{gathered} MnO_2 + 4\,HCl \longrightarrow 2\,H_2O + MnCl_2 + Cl_2, \\ MnO + 2\,HCl \longrightarrow H_2O + MnCl_2. \end{gathered}$$

If manganous salts are oxidized in the presence of a base, manganese assumes the valence of 6 (as in MnO_3) and manganates are produced, exactly as was true in the case of chromium. This is illustrated as follows:

$$MnCl_2 + O_2 + 4\,NaOH \longrightarrow 2\,NaCl + Na_2MnO_4 + 2\,H_2O.$$

This is equivalent to stating that any oxides of manganese heated in the air with a strong base tend to take up oxygen and yield derivatives of the two highest oxides.

The manganates are very unstable, differing from the chromates in this respect, tending to break down to manganese dioxide:

$$2\,K_2MnO_4 \longrightarrow 2\,K_2O + 2\,MnO_2 + O_2.$$

Naturally, this action takes place more rapidly if acid is present to take up the alkali, K_2O, and thus start the decomposition. Even the weak carbonic acid of the air is sufficient to precipitate the brown oxide from the green manganate solution. On the introduction of any dilute acid into such solutions, the active oxygen released helps oxidize other molecules of the manganate into the permanganate:

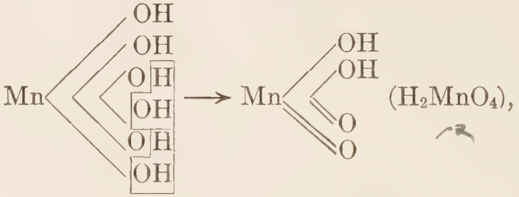
$$\begin{gathered} K_2MnO_4 + CO_2 \longrightarrow K_2CO_3 + MnO_2 + O, \\ 2\,K_2MnO_4 + O + CO_2 \longrightarrow 2\,KMnO_4 + K_2CO_3. \end{gathered}$$

Thus the green manganate solution changes into the purple permanganate. Ozone is now being used to oxidize the manganate.

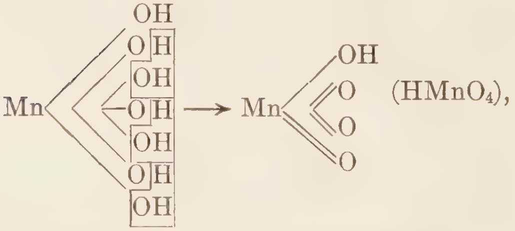
In the manufacture of ***potassium permanganate,*** black manganese dioxide is fused with potassium hydroxide and potassium chlorate. The fused mass is dissolved in water, forming a green manganate solution, which is then transformed by carbonic acid or ozone, changing rapidly to a purple color. The permanganate is crystallized from the solution after filtering off some manganese dioxide which is put through the process again.

$$2\,K_2MnO_4 + O_3 + H_2O \longrightarrow 2\,KMnO_4 + O_2 + 2\,KOH.$$

If we consider all oxygen acids as hydroxides of the nonmetallic element, the structure of manganic and permanganic acids is easily represented. The anhydride of manganic acid is MnO_3 ($H_2MnO_4 \longrightarrow H_2O + MnO_3$), and therefore the valence of the manganese is 6. A mother acid, $Mn(OH)_6$, may be imagined. It is too unstable to be isolated. By the same logic permanganic acid should be derived from a parent acid, $Mn(OH)_7$.



Parent acid ⟶ manganic acid.



Parent acid ⟶ permanganic acid.

Permanganates as Oxidizing Agents.—Potassium permanganate is very commonly used as a strong oxidizing agent. The organic matter in drinking water is oxidized completely by boiling the water after the addition of a very dilute solution of this substance. The reduction of the permanganate amounts in effect to dropping from the oxide Mn_2O_7, to one of the lower oxides, MnO_2, or MnO. The extent of the reduction, and the answer to the

$3Na_2SO_3$ + [illegible]

$3N$ [illegible]

question which oxide will be formed, is determined by whether the reduction takes place in basic or acid solution. In basic or neutral solution manganese dioxide is formed; and in acid solution, the lowest oxide, MnO, which acts most strongly basic. Of course manganous oxide, MnO, would react at once with any acid present to form manganous salts.

If to a solution of a permanganate, sulfurous acid is added, the manganese is reduced to a valence of 2, to MnO; five atoms of oxygen are removed by the sulfurous acid and five molecules of sulfuric acid are produced by the reciprocal oxidation. This acid produced is useful in removing the base present, K_2O, and then in removing the base produced, 2 MnO. The equations may be given in detail and summarized as follows:

(1) $2\ KMnO_4\ (\text{or}\ K_2O \cdot Mn_2O_7) + 5\ H_2SO_3 \rightarrow K_2O + 2\ MnO + 5\ H_2SO_4,$

(2) $K_2O + H_2SO_4 \rightarrow K_2SO_4 + H_2O,$

(3) $2\ MnO + 2\ H_2SO_4 \rightarrow 2\ MnSO_4 + 2H_2O,$

(4) Summary: $2\ KMnO_4 + 5\ H_2SO_3 \rightarrow K_2SO_4 + 2\ MnSO_4 + 3\ H_2O + 2\ H_2SO_4.$

COMMON OXIDIZING AGENTS[1]

OXIDIZING AGENT	REDUCTION PRODUCT	VALENCE CHANGE	ELECTRONS GAINED BY THE OXIDIZING AGENT
KNO_3 (fused).....	KNO_2	$N^{5+} \rightarrow N^{3+}$	2 (−)
$KClO_3$ (fused)....	KCl	$Cl^{5+} \rightarrow Cl^{1-}$	6 (−)
MnO_2 (fused).....	$MnSiO_3$	$Mn^{4+} \rightarrow Mn^{2+}$	2 (−)
HNO_3...........	NO_2	$N^{5+} \rightarrow N^{4+}$	1 (−)
HNO_3...........	NO	$N^{5+} \rightarrow N^{2+}$	3 (−)
HNO_3...........	NH_4NO_3	$N^{5+} \rightarrow N^{3-}$	8 (−)
H_2SO_4...........	SO_2	$S^{6+} \rightarrow S^{4+}$	2 (−)
H_2SO_4...........	S	$S^{6+} \rightarrow S^{\circ}$	6 (−)
H_2SO_4...........	H_2S	$S^{6+} \rightarrow S^{2-}$	8 (−)
Cl_2..............	2 HCl	$Cl_2^{\circ} \rightarrow 2\ Cl^{1-}$	2 (−)
HClO............	HCl	$Cl^{1+} \rightarrow Cl^{1-}$	2 (−)
$HClO_3$...........	HCl	$Cl^{5+} \rightarrow Cl^{1-}$	6 (−)
$HClO_4$...........	HCl	$Cl^{7+} \rightarrow Cl^{1-}$	8 (−)
$FeCl_3$ (acid)......	$FeCl_2$	$Fe^{3+} \rightarrow Fe^{2+}$	1 (−)
KNO_3 (acid)......	NO	$N^{5+} \rightarrow N^{2+}$	3 (−)
H_2O_2.............	$2\ O^{2-}$	$O_2^{2-} \rightarrow 2\ O^{2-}$	2 (−)
$K_2Cr_2O_7$..........	$Cr_2(SO_4)_3$	$2\ Cr^{6+} \rightarrow 2\ Cr^{3+}$	6 (−)
$KMnO_4$ (acid)....	$MnSO_4$	$Mn^{7+} \rightarrow Mn^{2+}$	5 (−)
MnO_2 (acid)......	$MnSO_4$	$Mn^{4+} \rightarrow Mn^{2+}$	2 (−)
$KMnO_4$ (base)....	MnO_2	$Mn^{7+} \rightarrow Mn^{4+}$	3 (−)
K_2CrO_4 (base)....	$KCrO_2$	$Cr^{6+} \rightarrow Cr^{3+}$	3 (−)
KClO (base)......	KCl	$Cl^{1+} \rightarrow Cl^{1-}$	2 (−)

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[1] From Brinckley's *General Chemistry* (The Macmillan Co.).

Solutions of permanganate are so often titrated against reduced iron salt solutions that it is convenient to give the concentration as for example, "1 cc. $KMnO_4$ solution oxidizes 0.00158 g. of iron from the ferrous to the ferric condition." It is evident that this oxidizing power varies from acid to basic solution.

Tests.—It is easy to recognize manganese compounds by melting them with potassium hydroxide and a little potassium nitrate or chlorate. The green color of the manganate formed is characteristic.

$$MnO_2 + 2\ KOH + (O) \longrightarrow K_2MnO_4 + H_2O.$$

A few drops of a solution of a manganese salt may be boiled with nitric acid and a little lead peroxide added (while holding the tube over a waste jar). On settling, pink permanganic acid may be seen. Both tests are remarkably delicate.

EXERCISES

3. In what alloy is chromium valuable? What is the chief chromium ore? Where mined?
4. What are the differences between chromic salts and chromates?
5. What is the usual test for a chromium compound?
6. How can we change a manganate to a permanganate?
7. How does potassium permanganate oxidize sulfur dioxide in water solution to sulfuric acid?
8. Using the chart of "Common Oxidizing Agents" and reviewing the examples (pages 181 and 182) quoted from Brinckley's test, write the oxidation-reduction equations applying to $K_2Cr_2O_7$ and $KMnO_4$.
9. How many liters of H_2S are necessary to decolorize a solution containing 12.5 g. of potassium permanganate and some sulfuric acid?
10. How much iodine will be liberated when 5 g. of $K_2Cr_2O_7$ are treated with excess potassium iodide and H_2SO_4?
11. What weight of SO_2 will be oxidized by 50 g. $KMnO_4$ in alkaline solution? In acid solution?
12. What weight of HCl (in terms of the gas) will be oxidized by 50 g. of $K_2Cr_2O_7$? How many liters of Cl_2 will be liberated?

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"Chromium Plating," *J. Chem. Ed.*, *6*, 1355, (1929).

CHAPTER XLVI

IRON, COBALT, AND NICKEL

	Atomic Weight	Density	Melting Point	Oxides
Iron	55.84	7.8	1510°	FeO, Fe_2O_3, Fe_3O_4
Cobalt	58.94	8.5	1478°	CoO, Co_2O_3, Co_3O_4
Nickel	58.69	8.8	1452°	NiO, Ni_2O_3, Ni_3O_4

These three elements occupy a position in the periodic table following manganese, somewhat as a bridge between two octaves or periods of the table. Their valence might be expected to reach 8, but each of the three elements displays valences of 2, 3, and 4. However, in nickel carbonyl, $Ni(CO)_4$, and iron carbonyl, $Fe(CO)_4$, there is some suggestion of a valence of 8. There is no vertical column relation between these three elements (as in the halogens). Rather, they occupy the position of a single element. They are all magnetic, all have high melting points, and all decompose water at high temperatures.

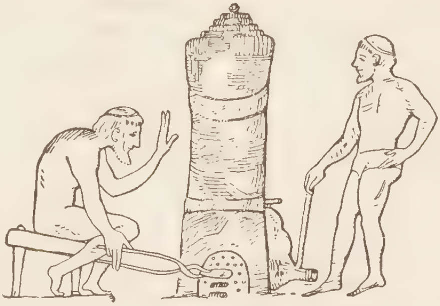


FIG. 158.—An ancient Greek stack furnace.

IRON

Iron was probably known in the period 3000–4000 B.C. and it was certainly used for weapons and tools by the Hebrews and Assyrians as early as 1400 B.C. Yet in Homer's time (about 900 B.C.) Greece still considered iron as rare.

Occurrence.—Free iron in nature is rare. A little occurs in Greenland and a little is found in meteorites. These star fragments are largely iron mixed with 3–8 per cent nickel and sometimes a little cobalt. The most important iron ores are oxides, although the English ore is a carbonate. Iron pyrites, FeS_2, is mined as a source of sulfur rather than of iron. Hematite, Fe_2O_3, furnishes the world with, by far, the greater part of its iron. Limonite, $2\,Fe_2O_3 \cdot 3\,H_2O$, is a yellowish ore, while magnetite, Fe_3O_4, is a black oxide supplying only 5 per cent of the world's iron. In addition to the workable ore beds there are iron oxides in clays to add to the beauty of coloring so conspicuous in Yellowstone Park and elsewhere. Bricks owe their colors to such oxides. Without the iron compound known as hæmoglobin the blood could not function properly.

The United States is the most fortunate country in the world in the location and richness of iron ore deposits. Before the war, Germany was second and England third, but with the winning of Lorraine, France has taken from Germany her largest ore beds and now is second only to the United States in the richness of her iron ore deposits. Sweden has important ore beds, as have Russia and Morocco. China is rich in iron, but the industry is only in its infancy there. Canada mines and smelts a good deal of iron ore. It seems probable that the largest and richest iron ore deposit yet discovered is located in Brazil. At present it is almost inaccessible, but in time it will be tapped by railroads.

Metallurgy.—Carbonates of iron are converted into oxides on roasting, and oxides are reduced by heating in contact with coke and limestone. The raw materials are used in such enormous quantities that the location of steel cities like Pittsburgh and Gary depends upon relative freight costs. The marvelously cheap freight rates on the Great Lakes have a vital influence on the location of steel centers. Huge ore boats carry 13,000 tons of ore at a load, at a cost of about one sixth that by rail. These boats are loaded in 20 minutes and unloaded in 4 hours.

The greatest worked ore bed in the world is found around the western end of Lake Superior. A large deposit occurs in Alabama, another in New York, another in Colorado, and several in California. California lacks coal, but is rich in fuel oil and water power. By a combination of electric furnace heat and the reducing action of fuel oil this state may yet succeed in smelting her enormous deposits of iron ore.

The Blast Furnace.—Iron was made many centuries ago, but its manufacture on a vast scale did not become possible until 1619 when coal or coke was first used as the reducing agent. Yet during the first half of the last century charcoal was still in common use in American blast furnaces.

The modern blast furnace is of giant proportions (Fig. 159). Most of them are 90 ft. high and some are higher. The greatest diameter is usually about 20–25 ft. They are built of heavy steel plates lined with fire brick. The lower part where the heat is more intense is usually bound with water-cooled bronze blocks set in the brick wall. At the top of the "stack," as the furnace is called, are double bell-shaped doors which admit the ore, coke, and limestone without undue loss of gases. Below this point the stack steadily widens to allow for expansion of the charge. But at a certain point fusion of part of the material causes such a great decrease in volume that the stack tapers in accordingly. Otherwise the heavy charge would fall and burst the furnace. No doubt the correct angle of taper was learned by costly experience. The narrowing part is called the "bosh." Just below this is the "crucible" in which molten iron and slag accumulate.

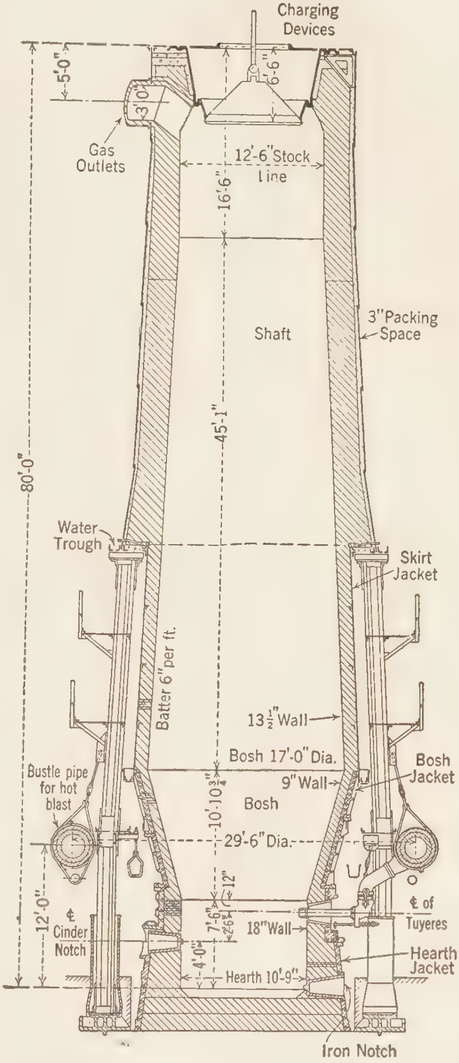

Charging Devices
5'-0"
3'-0"
6'-6"
Gas Outlets
12'-6" Stock line
16'-6"
3" Packing Space
Shaft
45'-1"
80'-0"
Water Trough
Skirt Jacket
Batter 6" per ft.
13½" Wall
Bosh 17'-0" Dia.
Bustle pipe for hot blast
9" Wall
Bosh Jacket
10'-10¾"
Bosh
29'-6" Dia.
12'-0"
12"
℄ of Tuyeres
℄ Cinder Notch
7'-6"
2'-6"
18" Wall
4'-0"
Hearth 10'-9"
Hearth Jacket
Iron Notch

FIG. 159.—The blast furnace.

The tap hole for iron is at the bottom, but the "cinder notch" for the slag is a little higher. Just above the crucible are several openings called "tuyeres," through which a great blast of heated air is blown to burn the coke. From 40,000 to 50,000 cubic feet of air per minute at 15 to 20 lbs. pressure is required.

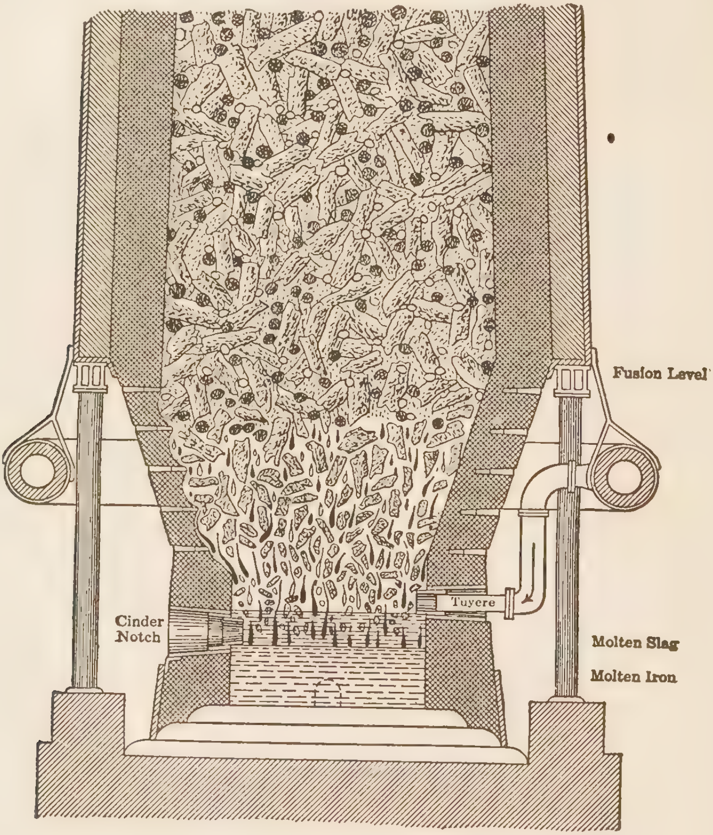


Fig. 160.—Lower portions of a blast furnace.

It may seem that hot carbon is the active reducing agent in the blast furnace, but the carbon monoxide formed is even more effective because it is a gas and hence comes in better contact with the ore. As the charge enters the stack, it soon reaches a temperature of 300° and as it settles to lower and hotter zones the reducing action of ~~carbon monoxide~~ (exothermic) becomes effective. At still lower zones and higher temperatures the limestone loses carbon dioxide and becomes calcium oxide, which unites with the alumina and silica of the ore to form a fusible slag. At this point the hot coke adds its reducing action (endothermic). The pasty particles of free iron do not melt until they have dissolved enough impurities, such as sulfur, silica, and carbon, to lower the melting point sufficiently. The melted iron runs in the crucible, while the lighter fluid slag floats on top (Fig. 158). At the top of the bosh the temperature is 1350° C. and at the top of the crucible about 1900° The equations representing the various reactions follow:

$$
\begin{aligned}
C + O_2 &\longrightarrow CO_2,\\
CO_2 + C &\longrightarrow 2\,CO,\\
Fe_2O_3 + 3\,CO &\longrightarrow 3\,CO_2 + 2\,Fe,\\
2\,Fe_2O_3 + 3\,C &\longrightarrow 3\,CO_2 + 4\,Fe.
\end{aligned}
$$

The iron is tapped off every 6 hours, but the slag is removed more frequently. The iron is run into molds from which the solid "pigs" are removed or it may be carried in great ladles to the steel mill without solidifying. Slag is carried away in ladles to the dump or is granulated by pouring into water. In this form it is easy to handle as railroad ballast or as a raw material for Portland cement. Since this is a complex calcium aluminum silicate slag needs only to be burned with more lime and ground to produce a very fair grade of hydraulic cement.

A great deal of fuel is wasted because of the moisture in the air blast, 224 gallons of water on an average July day carried in every minute by the 40,000 cubic feet of air. The Gayley process was once used to freeze out this moisture and furnish dry air at a saving of the coke. The gases from the top of the stack are worth saving. In composition they approximate producer gas and have a fuel value of 100 B. T. U. per cubic foot. There is a gain in using this gas at once because it leaves the stack at about 400°. This gas mixture is 24 per cent carbon monoxide, 16 per cent carbon dioxide, and 60 per cent nitrogen (from the air blast). It is led through a great pipe from the top of the stack to dust catchers and thence to the boilers, where it is burned to raise steam for the engines. It is more modern practice to explode this gas in gas engines. About one-third the stack gas is burned directly in "stoves." These are steel towers filled with an open checkerwork of fire brick, which becomes highly heated. The gas is then turned off and cold air blown through to the base of the stack. As soon as this stove chills the air is led through another hot stove. Usually each stack is accompanied by four stoves. It is necessary to preheat the air blast in order to secure the highest possible temperature in the blast furnace.

Blast furnaces work continuously for many months until the lining wears away. They produce from 500 to 600 tons of pig iron per day. Some large furnaces use 1000 tons of 56 per cent ore, 500 tons of coke, and approximately 250 tons of limestone and 1200 tons of air daily. Steel plants with their own by-product coke ovens use the coke in the blast furnace and the coal gas for their open-hearth furnaces.

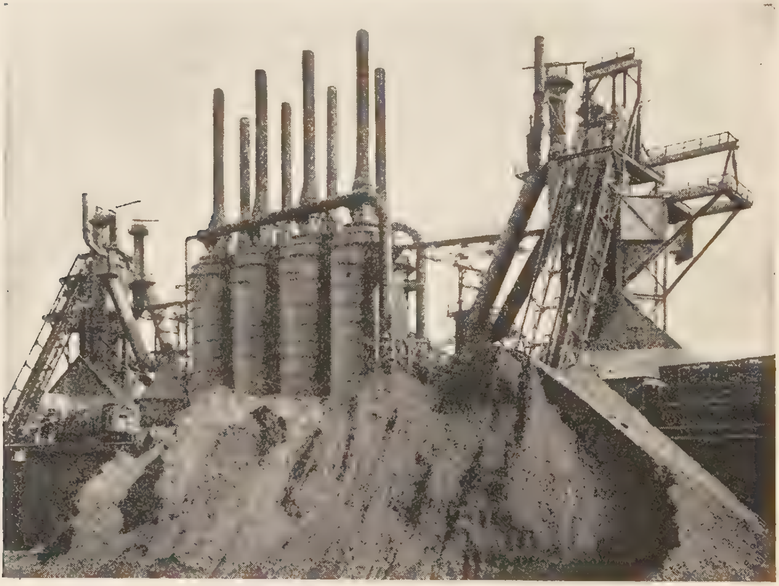


Fig. 161.—Two blast furnace "stacks" (with four "stoves" each for preheating the air blast), and a convenient ore pile.

In 1929 large scale experiments were in progress looking toward a revolution in iron manufacture. A mixture of coal and iron ore is heated in a coke oven, or in a long rotating tube. The coal burns by union with the oxygen of the ore. The iron does not melt after reduction, but comes out in a crumbly form ready for the process of steel making. The final result of this great experiment cannot be predicted at this time. If it succeeds low-grade ore and such cheap fuel as North Dakota liquite may be made available for the iron industry.

The Romans knew the art of making steel, but all forges were operated by a hand bellows, until comparatively recent times. Thus the furnace size was quite limited until the invention of the steam engine, which made possible the great blast of air now used, and so increased tremendously the size of the blast furnace.

Pig Iron.—The product of the blast furnace is termed ***pig iron.*** It is only about 92–94 per cent iron, the usual impurities being about 3 per cent carbon along with some sulfur, silicon, manganese, and phosphorus. Much of this iron is cast into pigs for convenience in handling and then shipped to the various markets. It is remelted at the foundries (by coke in a cupola) and cast into such shapes as are needed for radiators, stoves, wheels, and a thousand useful articles. Pig iron is cast iron, but there are two types, depending on the rate of cooling. If poured into a metallic mold so that the liquid is chilled suddenly, the carbon does not have time to separate as graphite, but remains uniformly distributed as cementite, Fe_3C. The product is white, very hard, and very brittle. If cooled more slowly in sand molds, gray cast iron results. In this, part of the carbon has had time to separate as graphite. It is not nearly so hard as the white variety and can be given some ductility if annealed a few days.

Such metal melts at about 1150°, while pure iron melts at about 1530°. Cast iron is hard, but low in tensile strength. It cannot be welded or forged, but it expands enough on cooling to completely fill the mold.

Cast iron has some useful properties not possessed by steel. Its high fluidity, which enables cast iron at comparatively low temperatures to fill intricate molds; its low shrinkage on solidifying; its ease of machining, due to the soft graphite flakes which lubricate the cutting tools; and its greater resistance to corrosion than steel, make it an unreplaceable metal. Admittedly, it has far less strength than steel and is very brittle under shock.

Soft cast iron owes its character to the 3 to 3.5 per cent of carbon, present largely as graphite. The manufacturer controls this amount of graphite mainly by the addition of silicon and by the rate of cooling.

Cast iron pipes laid in 1665 still supply water to the fountains of Versailles.

Wrought Iron.—To make a tough iron suitable for anchors, horseshoes, etc., it has long been the practice to purify melted pig iron on a bed of iron oxide in the *puddling furnace.* This is merely a small reverberatory furnace so built that heat is reflected and radiated down on the charge from the low roof of the furnace (Fig. 162). The pig iron melts, but as the impurities are burned out by the oxygen of the scale or ore on which it rests, its melting point rises and the metal becomes plastic rather than fluid. Limestone may be added as a flux. The metal is worked by the "puddler," using a long "rabble," and is finally removed in balls weighing about 100 pounds. Under the hammer or in the rolls the fluid slag is squeezed out, leaving nearly pure iron in fibers separated by thin films of slag. The product is extremely tough and strong, but not as hard as cast iron.

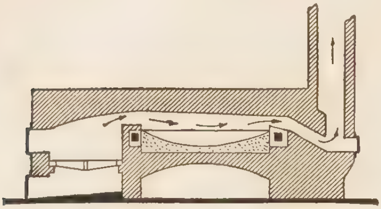


Fig. 162.—Puddling furnace.

In recent years wrought iron has been largely replaced by low-carbon steel (0.2 per cent carbon or less), which is just as tough and is made more rapidly.

In 1929 commercial efforts were made to produce wrought iron on a large scale by pouring melted pig iron into melted slag. The gases liberated caused the dispersion of the metal into fine drops. The iron-slag mixture was rolled in the usual way to reduce the slag content and give the mass tough fibrous structure. The quality of the product compares very favorably with that of hand-wrought iron.

Steel.—Impurities are usually things to be gotten rid of, but in the case of iron this idea has to be modified. Pure iron is far surpassed in useful properties by iron containing from 0.1 to 1.0 per cent of carbon, a product known as steel. Steel containing over 2 per cent carbon is brittle. Of late years, we have even gone so far as to add manganese, chromium, nickel, vanadium, tungsten, and other elements, so that some alloy steels contain four or five elements. Pig iron contains enough carbon to make a hard steel, but the sulfur, silicon, etc., are injurious and must be removed. The only way to do this is to oxidize everything but the iron. Volatile oxides are blown out and the others unite with ~~a~~ flux to form a fusible slag easily separated by gravity. This is usually done in a Bessemer converter or in an open-hearth furnace.

The Bessemer Process.—Wm. ~~Kelly~~, an American, proved in 1852 that the impurities in melted pig iron could be burned out by a blast of air. It was three years later that Bessemer, the Englishman, discovered and patented the same process. Although Kelly did not apply for patents until 1857, almost two years after Bessemer's English patent was granted, his application was allowed because he was able to prove that he had worked out the idea as early as 1847. This invention enormously increased the world's steel production and thus made possible the great era of railroad building that marked the latter half of the past century.

The Bessemer converter for iron is a huge steel egg lined with dolomite or siliceous rock, as desired. In a false bottom are many small holes. Below is the wind box into which air is forced through a hollow trunnion. The whole converter can be tilted to any angle. Molten iron is poured in while the converter is nearly horizontal, air turned on, and the converter raised. Air bubbling up from the small holes at 20 to 30 lbs. pressure oxidizes the carbon, silicon, sulfur, phosphorus, and manganese with so much evolution of heat that the iron becomes even more fluid. A dazzling flame and showers of sparks present a magnificent spectacle. After 15–20 minutes the impurities are oxidized and the converter tilted to pour its contents into a ladle, from which it is poured into a series of ingot molds. At the moment of pouring, the desired amount of carbon, together with manganese or other elements, is added to the ladle. Since there is much air trapped in pouring, there is danger of weak places in steel rails where such bubbles are found. It is customary to add deoxidizers, which unite with oxygen and form a light slag floating to the top. Manganese has long been used for this purpose, but in the last decade aluminum shot has become popular with the steel maker, as has silicon or rather ferrosilicon. Sometimes the deoxidizer is added just as the metal is poured.

At each "blow" 15 tons of steel are made, so the process is rapid, too rapid for the highest quality. Iron containing much phosphorus must be blown in a converter lined with dolomite or some other basic material. The phosphorus pentoxide formed reacts with this lining to form calcium and magnesium phosphates. In the United States the converters are usually "acid-lined," that is, faced with siliceous rock, since the ores usually contain very little phosphorus. The open-hearth steel, because of its superior quality, now leads in tonnage.

✱ **The Open-hearth Process.**—The open-hearth converter is a furnace with a wide, saucer-shaped hearth and a low roof (Fig. 163).

A charge of pig iron and rusty scrap is added with limestone sufficient for fluxing off the impurities. The fuel is producer gas or an oil spray burning above the charge. The air and gas are both preheated by passing through a checkerwork of fire brick.

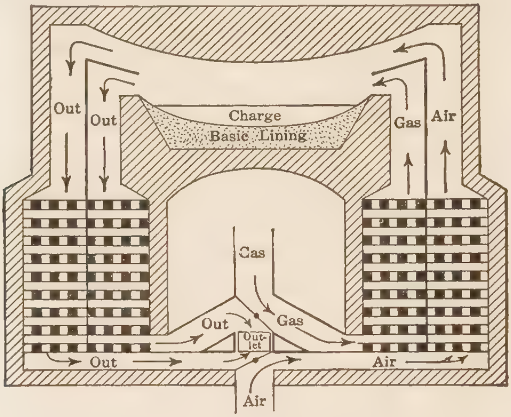


Fig. 163.—Open-hearth furnace.

The hot gaseous products of combustion pass off through another fire-brick chamber. By frequently reversing the direction of the gases great economy of heating is secured. This is the Siemens regenerative process. About 50 tons of steel are produced every eight hours. The process somewhat resembles the puddling process in that the oxygen needed is derived from rusty iron or a bed of iron ore. The necessary carbon, manganese, etc., are added at the moment of pouring. In this country open-hearth furnaces are lined with magnesite.

Exercise 1.—What metal would be best for fire bars—wrought iron or high-carbon steel? What metal would be best for wire?

The United States in 1929 produced 42,500,000 tons of the world's 85,000,000 tons of pig iron, and of steel over 50,000,000 tons out of a world total of twice that much. A large amount of steel is worked over from old "scrap," hence more steel than pig iron is produced. About 83 per cent of United States steel is the product of the basic open hearth and most of the remainder is from the silica-lined ("acid") Bessemer. An increasing amount is made in huge electric furnaces but the main difference from open hearth is the source of heat.

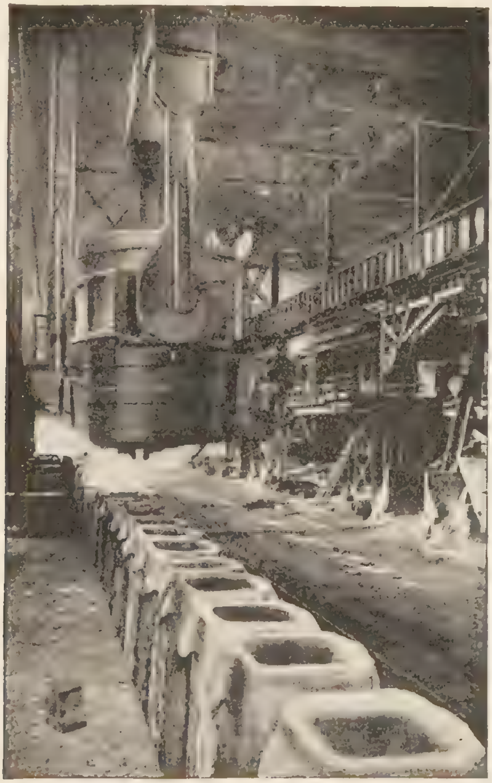
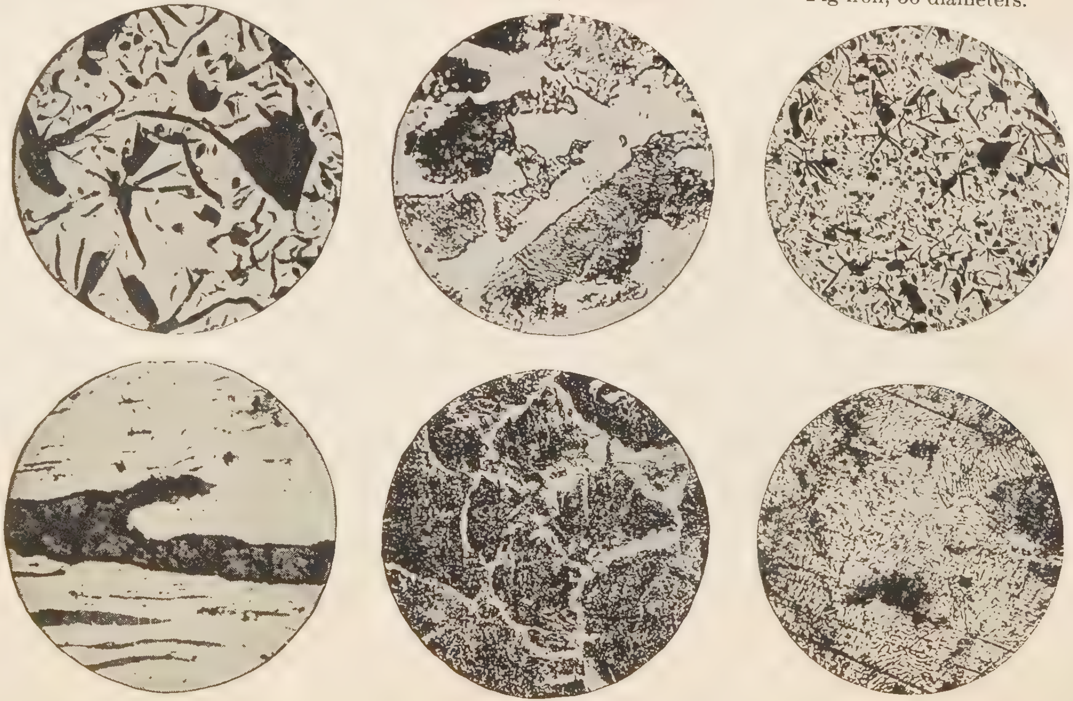


FIG. 164.—Tapping open-hearth steel from the ladle into the molds.

Crucible Steel.—Steel cut into scrap pieces is sometimes heated with the desired amount of carbon in small crucibles. A more uniform product, of better quality, and higher cost is obtained.

Cementation Steel is made very slowly by piling steel strips with carbon and heating hot enough to allow the carbon to diffuse slowly into the steel, but below the melting point.

The ancients knew something of crude cementation and crucible steel-making processes. By such methods were the Damascus and Toledo blades prepared. But during the Middle Ages the art was lost, to be revived in Belgium, in 1600, as far as the cementation process was concerned, and rediscovered in England, in 1742, as modern crucible steel making.



Pig iron, 125 diameters.

A commericial steel, slowly cooled from 850°, 500 diameters.

Pig iron, 36 diameters.

Wrought iron, longitudinal section, 125 diameters.

Same commercial steel, 0.5 per cent carbon, 125 diameters.

Steel, 0.9 per cent carbon, 500 diameters showing pearlite.

FIG. 165.—The above microphotographs of iron and steel were made by Professor James C. McCullough.

The Heat Treatment of Steels.—In steel above 900° the carbon is combined with part of the iron as cementite, Fe_3C. If cooled very suddenly, this remains in a solid solution in the rest of the iron and gives the steel its characteristic hardness. But if cooled more slowly, at about 700°, *cementite* crystals separate and appear in alternate layers or strata with the pure iron (*ferrite*). This mixture is called *pearlite* and has much of the softness and toughness of pure iron. A chilled tool can be reheated to any desired temperature and then cooled slowly enough to permit various crystalline arrangements to develop. This is tempering and by it any degree of hardness or toughness may be secured. The influence of such heat treatment on the structure of steels, and other alloys as well, is now studied by polishing the surface of the alloy, etching with chemicals that attack one compound more than another, and examining the etched surface with the microscope. This study is called metallography. Microphotographs of different steels show that their microstructure is far from homogeneous. The first use of metallographic analysis of metals in the detection of crime is recorded by J. H. Mathews.[1]

In case hardening a low-carbon steel is held for several hours in bone ash or gas at 1000° C.; carbon is taken up by the surface, yielding a steel that is hard on the surface and tough in the interior.

Properties of Pure Iron.—A single outstanding property of iron, magnetism, made possible the dynamo, motor, compass, telegraph, telephone, and other invaluable servants of mankind. The pure element has a density of 7.8 and is very ductile and malleable. It melts at about 1530°. It is not hardened by sudden cooling like steel. Chemically it is rather active, rapidly displacing hydrogen from acids. It rusts slowly in water (absence of air), displacing hydrogen. Weak acids, even carbonic, hasten this greatly. Consequently bases inhibit rusting. In moist air the metal rusts rapidly with formation of $2\ Fe_2O_3 \cdot 3\ H_2O$ as a loose, soft scale. Like manganese, iron is rendered passive when dipped in strong oxidizing acids. Passive iron will not displace copper from solutions of copper salts. Unfortunately its passivity is easily destroyed by a scratch or a shock.

The Rustproofing of Iron and Steel.—Galvanizing with zinc (page 535) or tinning (page 574) are well-known means of protecting iron or steel from rusting. A steel billet covered with copper may be drawn down to wire or a sheet on which the thin copper film is strongly adherent. A very little copper alloyed with steel greatly increases its resistance to corrosion, as of course does chromium (page 587). Steel shingles covered with lead are known. Structural steel imbedded in concrete never rusts. Nickel plating has long been practiced, while the very effective chromium plating is rapidly coming into general use.

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[1] *Ind. Eng. Chem.*, *15*, 595, (1923).

Protective oxide coatings on iron or steel are, in general, prepared by heating the metal in a suitable atmosphere or by oxidizing in the presence of certain aqueous or fused reagents. Repeated heatings alternately in oxidizing and reducing gases give a heavy, black coating of Fe_3O_4. Heating in air to 350° C. or above, sometimes in presence of superheated steam, also yields a coherent oxide layer. This is sometimes reduced by hydrocarbons to Fe_3O_4. Heating steel in a smoky flame or in volatilized oil has been tried.

Immersing steel in hot, dilute phosphoric acid, drying and oiling, is a common treatment. Chromates offer some protection. When steel is heated in air to form protective films various colors are produced, depending on the temperature.

TEMPER COLORS OF STEEL

TEMPER COLOR	° C.	° F.	TEMPER COLOR	° C.	° F.
Pale yellow	220	418	Purple	280	536
Straw	230	446	Pale blue	300	572
Brown	255	491	Dark blue	315	599

Alloy Steels.—We could not make autos for less than four times their present cost were it not for the modern development of alloy steels. Crankshafts, driving shafts, transmission shafts, axles, frames, and gears are stronger, tougher, lighter, and stand shocks and strains better because they are made of alloy steel. But some of these elements, and a number of others, are also added to form valuable alloys with the steel. In 1928 over 3,000,000 tons of alloy steel were made in the United States.

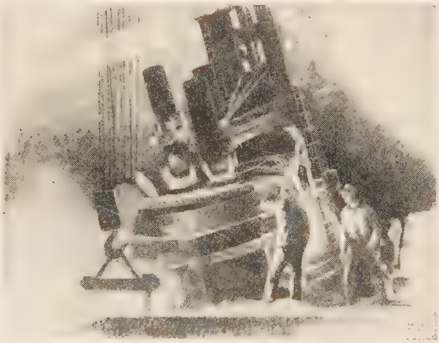

FIG. 166.—Pouring steel from an electric furnace.

Silicon, aluminum, manganese, and titanium are added to steels at the moment of casting as "scavengers," to remove air bubbles. Steel so cleansed is as much as 40 per cent stronger. But some of these elements, and a number of others, are also added to form valuable alloys with the steel. These alloy steels have brought about a series of revolutions in various industrial fields in which steel plays an important part.

Manganese Steel (12 to 14 per cent Mn) is very hard and tough. It is used in grinding machinery, rock crushers and burglar-proof safes.

Tungsten Steel (10 to 25 per cent W and 3 per cent Cr) is self-hardening; ~~that is~~, a tool of this material hardens on cooling in air without being quenched in oil or water. It also holds its temper when the tool is worked until red-hot from friction. Before the invention of this steel the speed of lathe work was seriously retarded by loss of temper in the cutting tools. Now the use of tungsten steel has multiplied several times the output capacity of the machine shops of the world.

EXERCISE 2.—What influence has carborundum had on the speed of machine shop work?

Vanadium Steel (0.1 to 0.4 per cent Va and 1 per cent Cr). When steel is desired to stand the heaviest shocks and vibrations, nothing is quite so effective as adding vanadium. Axles, cranks, frames, and piston-rods are made of this alloy. Vanadium steel rods can be twisted and bent double when cold.

"Chrome" Steel (2 to 4 per cent Cr). Chromium makes steel extremely hard. Cutting tools of special hardness, and armor plate are made of this alloy.

Nickel Steel (3.5 per cent Ni). This steel resists corrosion, is hard, elastic, and very suitable for armor plate, wire cables and propeller blades.

"Duriron" (15 per cent Si). This hard but brittle alloy resists the attack of hot concentrated nitric and sulfuric acids and so has many uses in chemical manufacture. It is difficult to machine.

Titanium added to the better steels to the extent of 1.10 per cent removes both oxygen and nitrogen. It is one of the few elements that burn in nitrogen. In steels it also facilitates removal of silicate inclusions by forming a slag with them. Its use is growing.

"Stainless Steel" containing about 15 per cent of chromium, when heat-treated and polished, has remarkable corrosion-resisting properties. If the alloy contains less than 0.12 per cent carbon it is called rustless or stainless iron. Both alloys are coming into extensive use in nitric acid plants.

Nitrided Steel.—Hot steel "cracks" ammonia gas and probably forms a nitride of iron on the surface. At any rate the hardest steel surface known is obtained by heating steel 21 hours at 525° C in a stream of ammonia gas.

FERROUS COMPOUNDS

Ferrous Chloride, $FeCl_2$, is prepared by dissolving iron in hydrochloric acid. From this solution it crystallizes as $FeCl_2 \cdot 4\ H_2O$, blue in absence of air, but green in presence of air. The anhydrous salt is made by passing dry hydrogen chloride over iron wire or filings. Since ferrous chloride is much more soluble than the sulfate, it is more convenient to set up hydrogen sulfide generators with hydrochloric than with sulfuric acid. Ferrous chloride is easily oxidized:

$$2\ FeCl_2 + Cl_2 \longrightarrow 2\ FeCl_3.$$

Ferrous Sulfate, $FeSO_4$.—Although ferrous sulfate can be made by the action of dilute sulfuric acid on iron, it is usually secured as a by-product of the pickling of iron and steel. Scale (oxide) is removed by immersion in dilute sulfuric acid. The ferrous sulfate formed is recovered from solution in large quantity. In some places heaps of moist iron pyrites are allowed to oxidize in the air and the ferrous sulfate formed leached out:

$$2\ FeS_2 + 7\ O_2 + 2\ H_2O \longrightarrow 2\ FeSO_4 + 2\ H_2SO_4.$$

The crystallized salt, $FeSO_4 \cdot 7\ H_2O$, is used in water purification because, when added to water with lime, the hydroxide formed drags down dirt and bacteria in settling. A small amount is used in making iron tannate ink.[1] These contain tannin, which with ferrous sulfate forms ferrous tannate, easily oxidized to black ferric tannate. However, a trace of sulfuric acid prevents this in the bottle. When applied to the paper, this free acid is neutralized by basic material present and the oxygen of the air converts soluble ferrous tannate into black and insoluble ferric tannate. To give immediate color to the ink a dye is added. In the last few years there has been a large demand for ferrous sulfate in the dye industry. The double salt, $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$, is not an alum. (Why?) It is very stable, while the simple sulfate oxidizes readily in the air. Solutions of ferrous sulfate often contain a yellowish precipitate which is basic ferric sulfate, $Fe\langle^{OH}_{SO_4}$. A strip of iron and a little free acid prevent this oxidation.

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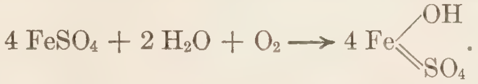
[1] *Removal of Ink Spots and Other Stains.* The *Scientific American* Supplement of Aug. 4, 1917 (page 71) gives a full discussion of the subject.



$$4\,FeSO_4 + 2\,H_2O + O_2 \longrightarrow 4\,Fe\langle^{OH}_{SO_4}.$$

Exercise 3.—Write the oxidation equations for the action of dilute nitric acid on ferrous sulfate in the presence of sulfuric acid. When dilute nitric acid oxidizes anything, it breaks up as follows: $2HNO_3 \rightarrow H_2O + 2NO + (3O)$.

Exercise 4.—Write the equations representing the oxidation of ferrous chloride by potassium permanganate in a dilute hydrochloric acid solution.

Ferric Compounds

Ferric Oxide, Fe_2O_3, and Hydroxide, $Fe(OH)_3$.—Hematite ore is Fe_2O_3, but a finer form, used as a pigment under the name Venetian red, is prepared by precipitation and ignition. Lime is added to a ferrous sulfate solution and the hydroxide allowed to oxidize in the air. Calcination of the product yields the oxide:

$$2\,Fe(OH)_3 \longrightarrow Fe_2O_3 + 3\,H_2O.$$

Ferric Hydroxide.—This gelatinous precipitate is thrown down when any soluble base is added to a solution of a ferric salt. It dissolves in acids but not in alkalies (unlike the hydroxides of chromium and aluminum). On drying this red-brown hydroxide loses water so gradually that it is probable it is merely a more or less hydrated form of the oxide, $F_2O_3 \cdot x\,H_2O$. On adding a concentrated solution of ferric chloride to boiling water, a rich red colloidal suspension of the hydroxide is formed. Hydrolysis is marked at 100°. (See chapter on Colloids.)

$$FeCl_3 + 3\,H_2O \rightleftarrows Fe(OH)_3 + 3\,HCl.$$

"Dialyzed iron" is a preparation of colloidal ferric hydroxide used sometimes as an antidote for arsenic poisoning.

The Ferrates.—The ferrates, for example, Na_2FeO_4, are salts of the unstable ferric acid, H_2FeO_4 which has not yet been isolated. In these ferrates, which in formula resemble sulfates, iron apparently has a valence of six. Potassium ferrate has been made by passing chlorine into a solution of potassium hydroxide in which ferric hydroxide is suspended. The ferrates are of very slight importance.

Ferric Chloride, $FeCl_3$.—The preparation of ferric chloride consists in passing chlorine into a solution of ferrous chloride. It is a yellow, deliquescent, and very soluble solid. It is hydrolyzed to such an extent that on heating it to dryness nothing but the oxide, Fe_2O_3, remains. The anhydrous form must be prepared by passing chlorine over rather hot iron. The salt sublimes on heating, so it is possible to measure its molecular weight at different temperatures. (How?) At 750° the formula must be $FeCl_3$, but at 450° the formula must be Fe_2Cl_6.

THE COMPLEX CYANIDES

Addition of potassium cyanide to a solution of a ferrous salt produces a precipitate of ferrous cyanide, readily soluble in an excess of the reagent:

$$FeSO_4 + 2\,KCN \longrightarrow Fe(CN)_2,$$
$$Fe(CN)_2 + 4\,KCN \longrightarrow K_4Fe(CN)_6.$$

The complex salt, potassium ferrocyanide, $K_4Fe(CN)_6$, ionizes as follows:

$$K_4Fe(CN)_6 \rightleftarrows 4\,\overset{+}{K} + \overline{Fe}(\overline{C}\overline{N})_6.$$

The ferrocyanide ion is very stable, yielding no simple iron ions. With ferric salts a precipitate called Prussian blue is formed. It is really ferric ferrocyanide:

$$4\,FeCl_3 + 3\,K_4Fe(CN)_6 \longrightarrow Fe_4[Fe(CN)_6]_3 + 12\,KCl.$$

When chlorine is passed into a solution of the yellow potassium ferrocyanide the reddish potassium ferricyanide is formed:

$$Cl_2 + 2\,K_4Fe(CN)_6 \longrightarrow 2\,KCl + 2\,K_3Fe(CN)_6.$$

This salt reacts with ferrous salts to form insoluble Turnbull's blue, which is ferrous ferricyanide:

$$3\,FeSO_4 + 2\,K_3Fe(CN)_6 \longrightarrow Fe_3[Fe(CN)_6]_2 + 3\,KSO_4.$$

Blue Prints.—Certain ferric salts in the presence of light are reduced to ferrous salts, so a paper soaked in ferric ammonium citrate and potassium ferricyanide and dried (all in a dark room) is subject to change on exposure to light. A design or drawing laid over this blue print paper allows light to reduce the ferric ammonium citrate to the ferrous salt wherever the paper is unprotected. On dropping the exposed paper into water the two salts dissolve and react to form Turnbull's blue. Where heavy lines in the drawing protected the paper there is no reduction by light and the salts are washed out, leaving white lines on a blue background.

Tests.—Ferrous salts are recognized by reaction with potassium ferricyanide to form Turnbull's blue. Ferric salts react with any alkali thiocyanate to form soluble, red ferric thiocyanate. They also react with potassium ferrocyanide to form insoluble Prussian blue. Ferric hydroxide is red, insoluble, and differs from the hydroxides of chromium and aluminum in not dissolving in sodium hydroxide.

Cobalt

Occurrence.—Cobalt was first prepared by Brandt in 1735 but has never become a very important element. It occurs in smaltite, $CoAs_2$, and cobaltite, $CoAsS$, as well as in a combination with nickel and arsenic. Canada produces 90 per cent of the world's cobalt. It is best prepared by the Goldschmidt process.

Properties.—The metal is hard and white like iron, yet it is also malleable and ductile. It melts at 1444° and has a density of 8.8. It displaces hydrogen slowly from ordinary dilute acids, but is readily attacked by nitric acid. It forms remarkable acid-resisting alloys with some other metals. A cobalt-aluminum alloy containing 12 per cent cobalt is 85 per cent stronger and 100 per cent harder than aluminum. For cooking utensils this new alloy has advantages since it is less easily corroded by acids and alkalies.

Alloys of the stellite type containing cobalt, chromium, and tungsten are rapidly coming into general use for cutting tools, even for high-speed work. Nearly all the cobalt produced is now being used in these alloys. Cobalt is also one of the main constituents of permanent magnets.

Oxides and Hydroxides.—Cobalt forms two series of compounds, like iron, with valences of 2 and 3. Cobaltous oxide, CoO, and cobaltic oxide, Co_2O_3, are the starting points for two series of salts. The ~~oxide Co_3O_4 is~~ really a sort of a salt like Fe_3O_4.

The black cobaltous oxide is used in giving a blue color to glass, enamels, and other silicates.

Exercise 5.—Cobaltous hydroxide is about as insoluble as magnesium hydroxide. Would it dissolve in ammonium salts?

Cobalt Salts.—Cobaltic salts are not stable (except the amines) but many cobaltous salts exist. They are all pink in solution, but when dry many of them turn blue. A ***sympathetic ink*** was made on that principle. The writing in the pale pink cobalt salt solution ($CoCl_2$, usually) was invisible, but on drying cautiously over a flame the blue color of the anhydrous salt became conspicuous.

Cobalt Sulfide, CoS.—Cobalt sulfide (like nickel sulfide) dissolves in dilute hydrochloric acid with such extreme slowness as to be practically insoluble and hence these two may be separated from the sulfides of iron, zinc, and manganese.

NICKEL

Occurrence and Preparation.—Nickel occurs associated with arsenic or sulfur, or both, as in nicollite, NiAs, and nickel glance, NiAsS. Canada produces 90 per cent of the world's nickel. The Ontario pentlandite is a sulfide of nickel, copper, and arsenic. Most ores carry some cobalt. The New Caledonia ore is a silicate of nickel and magnesium. The Ontario ores are roasted and run through a Bessemer process. The "matte," or melted mixture of sulfides of nickel, copper, and iron, is "blown" until the iron is removed in the slag, leaving the sulfides of nickel and copper. There are two or three methods of separating the nickel from the copper. By the Hybinette process the matte is roasted to remove the bulk of the sulfur and leached with 10 per cent sulfuric acid, which dissolves out most of the copper but very little of the nickel. The residue is melted and cast into anodes for purification by electrolysis. An alloy of copper and nickel obtained from the Ontario ores is used as "monel metal," a tough, ductile alloy which resists corrosion. It can be cast and machines well. Peas and beans contain traces of nickel.

A solid alloy (20 per cent Ni and 80 per cent Ag) is now coming into use for plumbing fixtures.

Properties.—Nickel is a white, magnetic metal resembling iron. It melts at 1452° and has a density of 8.8. It is hard, malleable, takes a high polish, and does not tarnish readily in the air. Hence many common metallic objects are nickel plated. Iron is first copper plated. Nickel has some use in alloys, such as monel metal, nickel steel, German silver, and nickel coins. Despite the white color our common 5-cent piece is 75 per cent copper and only 25 per cent nickel. Finely divided nickel is used as the catalyst in hydrogenating liquid fats to make solid fats. The chief use of nickel is in making nickel steel. Monel metal, a tough alloy of nickel and copper, very resistant to corrosion, is much used.

A new alloy ("permalloy") of 78.5 per cent nickel and 21.5 per cent iron with traces of other metals shows extraordinary magnetic permeability after receiving a special heat treatment. Its initial permeability is more than thirty times that of soft iron, consequently it is now used for submarine cables permitting five times the former speed of cabling. The copper cable is wrapped spirally with a narrow tape of permalloy.

"Perminvar," an alloy of nickel, cobalt and iron, is about to come into use as a spiral wrapping for submarine telephone cables. It becomes magnetized by the current flowing through the real cable.

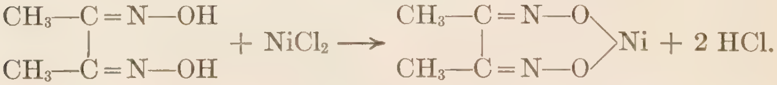
Nickel Compounds.—There are two series of nickel salts derived from nickelous oxide, NiO, and nickelic oxide, Ni_2O_3. All nickel salts are green when hydrated. Nickel sulfide, NiS, is precipitated as a black powder when ammonium sulfide is added to a solution of a nickel salt. Excess of the reagent peptizes it into a colloidal suspension that runs through the filter paper. Green nickelous hydroxide, $Ni(OH)_2$, is precipitated by addition of a base to a solution of a nickel salt, but if a hypochlorite be added to a nickel salt solution the black nickelic hydroxide, $Ni(OH)_3$, is thrown down.

Nickel Carbonyl, $Ni(CO)_4$.—This volatile liquid is formed when carbon monoxide is passed over nickel below 80°. The liquid boils at 43° and its vapor explodes at 60°. However, when diluted with carbon monoxide it decomposes gradually into nickel and carbon monoxide. By the Mond process (used in England) nickel ores are worked up to yield a finely divided metallic powder of nickel, copper, and iron. Carbon monoxide is passed over this powder at 50° to 80°, forming nickel carbonyl. This latter gas is then decomposed by passing it through a tower containing shot nickel heated to about 200°. Layers of nickel deposit on the shot, while the carbon monoxide liberated is returned to the carbonyl towers.

The Edison Storage Cell uses nickelic hydroxide and iron dust as the poles and a 21 per cent solution of potassium hydroxide as the electrolyte. On discharge the trivalent nickel is reduced to the divalent form while iron is oxidized to the divalent form. The action is reversed on charge. The voltage of this cell is lower than that of the common lead storage cell, but Edison's cell (p. 585) is lighter and more durable.

TESTS FOR NICKEL AND COBALT

Nickel salts react with dimethylgyoxime to give a scarlet precipitate.



$$\begin{array}{l}\mathrm{CH_3-C=N-OH}\\ \qquad\;|\\ \mathrm{CH_3-C=N-OH}\end{array} + \mathrm{NiCl_2} \longrightarrow \left.\begin{array}{l}\mathrm{CH_3-C=N-O}\\ \qquad\;|\\ \mathrm{CH_3-C=N-O}\end{array}\right\rangle \mathrm{Ni} + 2\,\mathrm{HCl}.$$

Cobalt compounds give a blue bead with borax or microcosmic salt, while nickel compounds yield a brown bead in the oxidizing flame. Cobalt salts react with nitroso-β-naphthol to yield a brick-red precipitate and in the presence of ammonia, with phenylthiohydantoic acid to yield a red-brown precipitate.

EXERCISES

6. What goes on in a blast furnace? What elements are in the pig iron?
7. How is open-hearth steel made?
8. What would we do without if we had no alloy steels?
9. Has cobalt any real uses? Has nickel?
10. How do we test for cobalt and for nickel?
11. What is the simplest formula of an iron oxide which contains 27.6 per cent oxygen and has a molecular weight of 232?
12. What weight of charcoal must be added to 6 tons of pure, melted iron to make a steel containing 2 per cent carbon?

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CHAPTER XLVII

VANADIUM, MOLYBDENUM, TUNGSTEN, AND URANIUM

Vanadium.—Peru has almost the only workable deposits of vanadium ore and these are covered with perpetual snow at an elevation of three miles. Pure vanadium is not easy to prepare and there are as yet, no uses for the pure metal. Reduction of vanadium pentoxide by metallic calcium with addition of calcium chloride in an electric furnace has recently proved a successful method for preparation yielding the metal of 99.9 per cent purity. Its ores are reducible at high temperatures, but the free element combines with most reducing agents as well as with nitrogen. Reduction by carbon in a vacuum furnace is the usual practice. The element is silvery white, very hard, and rather brittle. It melts at 1720° and has a density of 6.02. When added to steel it makes the alloy harder and greatly increases its tensile strength. Such an alloy is in demand for auto axles, airplane parts, locomotive tires, and for high-speed tool steel. It has thus contributed immeasurably to our comfort and safety and to our in-

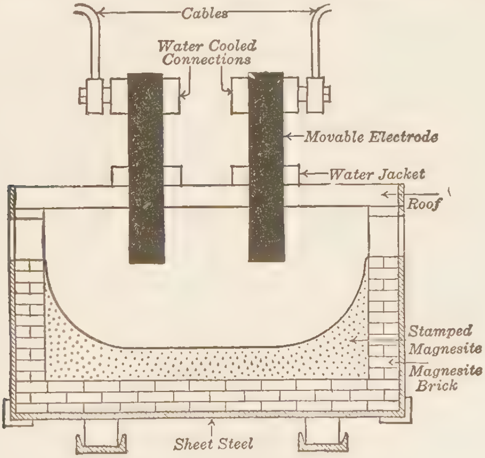
Cables
Water Cooled Connections
Movable Electrode
Water Jacket
Roof
Stamped Magnesite
Magnesite Brick
Sheet Steel

FIG. 167.—Electric furnace.

dustrial advance. Ferrovanadium is easier to prepare than vanadium itself and is the form used in the steel industry. This alloy is made by heating a mixture of vanadium oxide or sulfide, iron filings, and coke in an electric furnace (Fig. 167). Vanadium pentoxide, V_2O_5, is a valuable catalyst (p. 251).

This element forms a series of compounds on which the vanadium shows variable valence.

It has been suggested that the action of vanadium compounds in catalyzing the oxidation of sulfur dioxide may be

$$V_2O_5 + SO_2 \rightarrow V_2O_4 + SO_3,$$
$$2\ SO_2 + O_2 + V_2O_4 \rightarrow 2\ VOSO_4,$$
$$2\ VOSO_4 \rightarrow V_2O_5 + SO_2 + SO_3.$$

Molybdenum.—Molybdenum occurs chiefly as molybdenite, MoS_2, a black lustrous mineral resembling graphite, but twice as heavy. Colorado operates the largest molybdenum property in the world. The ore contains only one per cent of molybdenite which must be concentrated by the oil flotation process (p. 471). The element is usually prepared by the Goldschmidt process or by reduction with a cerium alloy. It is silvery white, melts at 2500°, and has a density of 8.6. Ferromolybdenum, the form in which the element is added to steel, is prepared in the electric furnace by heating a mixture of molybdenum ore, coke, and iron. Steels carrying a very small proportion of molybdenum and some chromium possess remarkable tensile strength and are used for crankshafts, axles of busses, and in airplane motors. Molybdenum itself can be tempered and forged like iron. Also like iron it takes up carbon when hot. The element finds some use in dental tooth plugs, in supports for tungsten filaments in lamps, in electron tubes, and in high-temperature resistor furnaces.

Molybdenum Compounds.—On roasting the sulfide, MoS_2, the ***trioxide,*** MoO_3, is formed. This is a yellow-white powder which dissolves readily in sodium hydroxide with formation of ***sodium molybdate,*** Na_2MoO_4. If ammonium molybdate solution is poured into dilute nitric acid, ***molybdic acid*** is formed. This reagent is used to precipitate orthophosphates as the yellow precipitate $(NH_4)_3PO_4 \cdot 12\ MoO_3 \cdot x\ H_2O$. This is the usual procedure in all analytical determinations of phosphorus. The composition of this yellow precipitate is so variable that it is more accurate to dissolve it in ammonium hydroxide and reprecipitate as $MgNH_4PO_4$, which is then dried and ignited to be weighed as $Mg_2P_2O_7$.

Tungsten.—Tungsten is now considered one of the "key metals" of industry, occupying fifth place among the first ten essential metals of modern civilization. Tungsten was discovered by Scheele in "scheelite" or calcium tungstate in 1781 and is supposed to have been a constituent of the historic "Damascus blades"—unknown to the makers. The chief ore is ferrous manganese tungstate, $FeMnWO_4$, called wolframite. (The Germans insist on calling the element "wolfram" and all chemists agree on W as the symbol.) Before the war most of the ore came from China, but after this source of supply was shut off the price soared to thirteen times the pre-war mark and production in California and Colorado was stimulated. In 1918, the United States produced over 5000 tons of tungsten. After the war prices fell and the easily-mined Chinese ores once more led in the world's markets.

Wolframite is fused with sodium carbonate and the sodium tungstate, $Na_2WO_4 \cdot 2\,H_2O$, formed is extracted with hot water. When this salt is treated with acids the free tungstic acid, $H_2WO_4 \cdot H_2O$, is precipitated. On ignition the oxide, WO_3, is secured. This oxide may be reduced by carbon or by the Goldschmidt process, but most of it is reduced by hydrogen in an electrically heated furnace at 1000°, or above.

Properties.—Tungsten has the highest melting point of all the metals, 3370°. Only carbon has a higher melting point, but carbon at high temperatures has a greater vapor pressure than tungsten. Tungsten is steel-gray, very hard, and very heavy with a density of 18.64. The metal is obtained as a powder on reduction of the oxide and must be worked into strong filaments or rods. This was a great problem. Melting (at 3370°) is not practicable and moreover the melted product becomes brittle when cold. It has been found that the only way to secure strong compact tungsten is to work it while very hot, but not melted. The reduced powder is compressed to brittle bars which are heated by electric resistance furnaces in a reducing atmosphere of hydrogen to about 1500°. The bars are taken out, smoking in the air, and worked in a swaging machine, which draws them down gradually to smaller and smaller rods. With repeated heating and working, the metal becomes stronger and more malleable. If desired for sheet, it is hammered and rolled, but if desired for wire it is drawn finer and finer until it is strong enough to be pulled through diamond dies to the diameter needed for lamp filaments. It is usual to draw it through 100 dies, each a shade smaller than the previous one.

The brittleness of tungsten which for so many years interfered with the use of this metal as a lamp filament was due to oxygen and carbon impurities. Pure tungsten, after elongation by drawing so as to develop long thread-like crystals, is soft and ductile. In many respects tungsten is superior to steel. It never rusts and is not attacked by acids cold. Tungsten is attacked by fused nitrates, peroxides, alkali carbonates, and caustic alkalies, but not by solutions of them. It is even very resistant to concentrated acids.

Tungsten lamp filaments are saving the people of this country over a billion dollars each year. The old carbon filaments used 3.25 watts per candle power, while the modern tungsten lamp uses less than 1.25 watts for the same illumination. We use 300,000,000 of these lamps annually.

High-speed steel cutting tools contain 18–20 per cent tungsten. Since these tools can be worked on the lathe until red hot without losing the necessary hardness, their use means an enormous saving in machine shop expense. Cady observes that one man at a lathe with tungsten steel tools can do the work formerly done by five men with five tools at five lathes. He also believes that high-speed tools have reduced the cost of automobiles considerably. And yet it is not long since tungsten was a "rare" element!

In the automobile industry tungsten is used in springs, axles, valves, steering apparatus, magnetos, etc. Tungsten phonograph needles are in common use. Tungsten steel rails wear longest. Permanent steel magnets contain some tungsten to increase their magnetic retentivity. Tungsten contact points are used by the million.

Tungsten Compounds.—There are four chlorides, WCl_2, WCl_4, WCl_5 and WCl_6. The hexachloride is formed by passing chlorine over tungsten at 300°. The others are secured by reduction of the hexachloride. The most important oxides are WO_2 and WO_3. Sodium tungstate, $NaWO_4$ is the best known salt. It is used in dyeing and in fireproofing fabrics and in making X-ray screens. Many complex tungstates are known.

Tungsten Carbide (W_2C), with some cobalt was developed in 1928 as the hardest cutting tool material yet manufactured (" *carboloy* ").

Common hardened tool steel has an average hardness on the Brinell scale of 850, while carboloy runs to 2000 and above. Without cobalt it has a strength of 50,000 pounds per square inch, but with cobalt carboloy reaches a strength of 275,000 pounds. Since it has no "temper" (holds its hard cutting edge in spite of the great heat of friction on the lathe) and is harder than any metals or alloys it may be asked to cut, its usefulness in machine shops will be very great. It cuts sapphire, which is next to the diamond in hardness.

Uranium.—Pitchblende, mainly uranium oxide, U_3O_8, with a little of many other elements present is a uranium ore found in Bohemia and Cornwall. Carnotite, a uranate and a vanadate of potassium, $K_2O \cdot 2\,UO_3 \cdot V_2O_5 \cdot 3\,H_2O$, is found in Utah and Colorado.

Uranium is a white metal, melting at about 1500°. Its density of 18.68 ranks it as one of the heaviest elements. It slowly oxidizes in the air and dissolves in the common acids. The element is prepared by reduction of the oxides with carbon in the electric furnace. Uranium was once used as one of the catalysts in the Haber process of making ammonia. The Belgian company extracting radium from a uranium ore (Kongo) sells uranium as a by-product to the glass and ceramic industry.

There are numerous oxides of uranium, easily changed from one to another, reminding us in many respects of the chemistry of chromium. The colors produced by uranium compounds in glasses and glazes are yellow, orange, red, green, and black.

Radium, which properly belongs in this group, is discussed on pages 268–274.

Tantalum is another illustration of a rarely used metal suddenly coming into considerable commercial use. Its density is 16.6 and its melting point 2770° C., but its most interesting property is its great resistance to chemical attack by hot nitric or hydrochloric acids or their mixtures and anything but the most drastic attack by sulfuric acid or sodium hydroxide. Hydrofluoric mixed with nitric acid quickly converts the metal into the fluoride.

If tantalum is heated in the air, the surface becomes blue at a temperature of about 400° C., and at a somewhat higher temperature, nearly black. Above a dull red heat the white oxide is produced, and the metal gradually burns. This metal combines with avidity with hydrogen, oxygen, or nitrogen. It will take up 740 times its own volume of hydrogen, producing a very coarse-grained, brittle product.

Tantalum containing dissolved gases will be harder than the pure metal, and if their quantity is appreciable the metal may even be brittle—so all annealing or heating operations with tantalum must be carried out in a vacuum.

Because of its ability to take up hydrogen and the gases of the air it is used as the structural and electrode elements in electron vacuum tubes as well as for filament and as a "getter" for freeing vacuum tubes from gas.

The most important use of the metal so far developed is as an electrolytic valve. In common with some other metals it has the quality of allowing current to pass through in only one direction when immersed in acid. This makes it possible to install a battery and rectifier as a permanent complete unit furnishing D.C. current from an A.C. source, for radio and industrial purposes.

Titaniferous iron ores often contain appreciable amounts of vanadium which in the magnetic concentrating process will follow the magnetite into the concentrate. The vanadium is present in the form of a ferro-vanadate which is readily decomposed by roasting, the vanadic acid then being oxidized to higher oxides that can be dissolved by acids.

EXERCISES

1. Calculate the percentage of tungsten in calcium tungstate? In wolframite?
2. How does tungsten serve humanity?

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CHAPTER XLVIII

THE PLATINUM METALS

	Atomic Weight	Density	Melting Point	Oxides
Ruthenium	101.7	12.3	1900°	RuO, Ru_2O_3, RuO_2, RuO_4
Rhodium	102.9	12.44	1907°	RhO, Rh_2O_3, RhO_2
Palladium	106.7	11.4	1549°	PdO, PdO_2
Osmium	190.8	22.5	2200°	OsO, Os_2O_3, OsO_2, OsO_4
Iridium	193.1	22.41	2300°	Ir_2O_3, IrO_2
Platinum	195.2	21.5	1755°	PtO, PtO_2

In the final column of the periodic table are three groups of three elements each. One of these groups, iron, cobalt, and nickel, has been studied already. The platinum metals are rare and are found usually as the free elements. They occur in alluvial sands in the Ural mountains of Russia, in Colombia, South Africa, the Pacific coast states, Brazil, and Borneo. Platinum forms the greater part of the extracted grains or nuggets. Russia leads in production.

The present price trend of all the platinum metals is down.

Platinum.—It is unfortunate that this element is so rare, for it is most useful. In 1906 it was on a par with gold but now it is worth more than five times as much as gold. Its high melting point, 1755°, its resistance to chemical corrosion, and its remarkable powers as a catalyst make it almost indispensable. In the laboratory it is used in the form of crucibles, wire, and sheet. Certain precautions must be taken in its use, as it is attacked by chlorine and aqua regia as well as by fused alkalies. It also alloys with a number of easily reducible metals. When hot it is permeable to hydrogen, so easily reduced compounds of certain metals should not be heated in platinum dishes over a gas flame. The coefficient of expansion of this metal is so near that of soft glass that it is used for leading-in wires in laboratory apparatus and in electric light bulbs. However, a cheaper alloy has been found for that purpose. Contact points for spark ignition were formerly made of platinum but now are made of the cheaper tungsten. It is easy to weld platinum at a red heat and in general it may be classed as rather malleable and ductile. It also conducts electricity moderately well.

When ammonium chloroplatinate, $(NH_4)_2PtCl_6$, is ignited a finely divided form of the metal called ***platinum sponge*** is secured. Heating asbestos soaked in chloroplatinic acid yields the metal in fine particles scattered through the asbestos. Such forms of platinum are used as catalysts in various industries, notably in the contact process of making sulfuric acid. The Ostwald process for oxidizing ammonia to nitric acid uses platinum gauze covered with reduced platinum in a spongy form. Oxygen is condensed on the surface of platinum, while hydrogen is actually dissolved in it. This explains why a platinum wire with spongy surface ignites an explosive mixture of oxygen and hydrogen. The gases are brought in closer contact, or activated, by the platinum. The vapor of methyl alcohol is ignited in the air by a fine platinum wire. Cigar lighters and gas lighters have been made on this principle.

In normal years Russia produced over 250,000 ounces, over 90 per cent of the world's output. Colombia in South America is the next largest producer, with Canada in third place. A newly-discovered lode of platinum ore in South Africa seems very promising.

The total production to date of about 11,000,000 ounces, has found its way into dental use, use in chemical apparatus, electrical apparatus and jewelry, and as catalyzing material. Platinum used in dentistry is lost to the world.

Women who use platinum jewelry at any time are taking from scientific use a metal for which there is no adequate substitute and of which there is never enough for scientific and industrial needs. White alloys, just as beautiful and durable, are available.

Compounds of Platinum.—Platinum forms two series of compounds with valence of 2 and 4. ***Platinum chloride,*** $PtCl_2$, is formed when chlorine is passed over the finely divided metal at 240°–250°. With hydrochloric acid it forms chloroplatinous acid, H_2PtCl_4. The potassium salt, K_2PtCl_4, is used in photography. Black platinous hydroxide, $Pt(OH)_2$, is formed by addition of a base to a solution of platinous chloride. On gently heating it yields the oxide and at higher temperatures the metal itself. Barium platinocyanide, $BaPt(CN)_4 \cdot 4\,H_2O$, fluoresces when bombarded by X-rays and hence is used for X-ray screens.

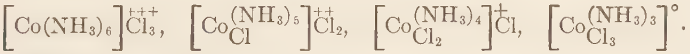
Platinum dissolves in aqua regia with formation of the soluble ***chloroplatinic acid,*** H_2PtCl_6. This is the reagent used in the quantitative determination of potassium, as the potassium salt, K_2PtCl_6, is insoluble. That the acid ionizes as follows:

$$H_2PtCl_6 \rightleftarrows 2\,H^+ + PtCl_6^{--}$$

is proved by addition of silver nitrate. No silver chloride is precipitated, only silver chloroplatinate, Ag_2PtCl_6.

Platinic Chloride, $PtCl_4$, is formed by heating chloroplatinic acid in a current of chlorine at 360° but is itself decomposed above 500°.

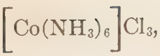
Werner's Coördination Theory.—The tendency of certain atoms (notably Pt, Co, Cr, Ru, Fe, Ni, Pd) to attach to themselves in a spatial arrangement a definite number of other atoms or groups or molecules was studied exhaustively by Werner. A good illustration of this was discussed in the comparison of the green and violet modifications of $CrCl_3 \cdot 6\,H_2O$ (page 590). Cobalt salts may also be cited here. Note below the series of ammonia complexes with $CoCl_3$.



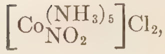
$$\left[Co(NH_3)_6\right]^{+++}Cl_3,\quad \left[Co\substack{(NH_3)_5\\ Cl}\right]^{++}Cl_2,\quad \left[Co\substack{(NH_3)_4\\ Cl_2}\right]^{+}Cl,\quad \left[Co\substack{(NH_3)_3\\ Cl_3}\right]^{\circ}.$$

Evidently NH_3 molecules can progressively displace the chlorine atoms to some other position in the molecule. At any rate, all the NH_3 molecules are held very closely by the central atom, cobalt, while some of the chlorine atoms may be ionizable and some not. It all depends on the existence of six groups spatially arranged around the central atom as at the corners of an imaginary octahedron and it doesn't matter much whether these six groups be six ammonia molecules, or five, plus one chlorine atom, or four plus two chlorine atoms, etc. In fact, in some of these complex compounds water may act as such a "coördination" group, or the nitro group (NO_2). Note however, the valence change in the series above. The $Co(NH_3)_6$ group forms a trivalent positive ion and in the first compound all three chlorine atoms will ionize. In the second, $Co(NH_3)_5Cl$ forms a divalent positive ion and only two of the three chlorine atoms will ionize. The final member is not an ion but a molecule with a zero valence.

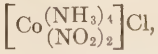
When a highly electronegative group such as NO_2 is substituted for chlorine atoms in the series below the comparative conductivity under comparable conditions decreases rapidly, practically to zero in the fourth member and then forces the coördinate complex to yield a negative ion.


$[Co(NH_3)_6]Cl_3$,

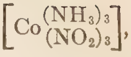
412


$\left[Co\begin{matrix}(NH_3)_5\\ NO_2\end{matrix}\right]Cl_2$,

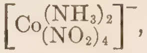
240


$\left[Co\begin{matrix}(NH_3)_4\\ (NO_2)_2\end{matrix}\right]Cl$,

97


$\left[Co\begin{matrix}(NH_3)_3\\ (NO_2)_3\end{matrix}\right]$,

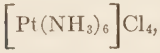
1.5


$\left[Co\begin{matrix}(NH_3)_2\\ (NO_2)_4\end{matrix}\right]^-$,

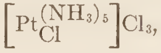
A negative
ion with good
conductivity

Another similar series with ammonia complexes of platinic chloride ($PtCl_4$) is given below, with comparative conductivities. Here the coördination number is four, less usual than six. The complex positive ion becomes a neutral molecule in the fifth member and a negative ion in the sixth and seventh members.

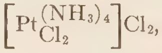
Werner emphasized the importance of the conception of six (sometimes four) atoms, groups, or molecules attached by non-ionized links to a central atom and of a change in the electrovalence when a group belonging to one of these types is replaced within the complex by one of the other types.


$[Pt(NH_3)_6]Cl_4$,

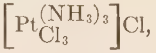
523


$\left[Pt\begin{matrix}(NH_3)_5\\ Cl\end{matrix}\right]Cl_3$,

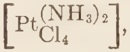
404


$\left[Pt\begin{matrix}(NH_3)_4\\ Cl_2\end{matrix}\right]Cl_2$,

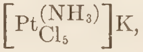
229


$\left[Pt\begin{matrix}(NH_3)_3\\ Cl_3\end{matrix}\right]Cl$,

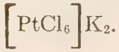
97


$\left[Pt\begin{matrix}(NH_3)_2\\ Cl_4\end{matrix}\right]$,

0


$\left[Pt\begin{matrix}(NH_3)\\ Cl_5\end{matrix}\right]K$,

108.5


$[PtCl_6]K_2$.

256

Palladium.—Palladium is associated with platinum in the natural alloys and resembles it in appearance and some properties. Yet it is more like silver in that nitric acid dissolves it. Then, too, it is softer, lighter, and melts more easily than platinum. In valence it resembles the other platinum metals. Its most interesting property is the ability of finely divided palladium to absorb 800 volumes of hydrogen—900 volumes if a strip of the metal is made the cathode of an electrolytic cell. It is remarkable that such adsorbed hydrogen displaces from solutions of their salts metals below it in the electromotive series, although a stream of hydrogen gas does not do so. Probably because of this activity of hydrogen adsorbed palladium sponge is used with hydrogen in organic reduction reactions. Palladium possesses such great resistance to the attack of oxygen, moisture, and hydrogen sulfide that it is sometimes used for the inner mechanism of watches, fine balance beams, surgical instruments, and special apparatus. It is used in soldering platinum and as a catalyst. Its present price is about $1.13 per gram.

Palladium dichloride, $PdCl_2 \cdot 2\,H_2O$, is made by dissolving the spongy metal in hydrochloric acid, a method that obviously must fail with platinum. The tetrachloride, $PdCl_4$, is not very stable. The salt, K_2PdCl_6, and the complex amines are suggestive of certain platinum compounds.

Rhodium.—Rhodium is not attacked by aqua regia or any acid, but reacts with chlorine. These are two chlorides, $RhCl_2$ and $RhCl_3$. Three oxides are known; RhO, Rh_2O_3, and RhO_2. the complex amines resemble those of cobalt. Rhodium is harder than platinum. A little rhodium alloyed with platinum improves that catalyst for the oxidation of ammonia.

We import 2000 oz. yearly to use in the manufacture of chemical apparatus, pens, pyrometers, etc.

Iridium.—This element resembles rhodium in its resistance to aqua regia. Since it is very hard and not oxidized at high temperatures it is useful for some apparatus and in the preparation of iridium-osmium alloy tips for fountain pens. When native platinum is warmed with aqua regia, only the platinum dissolves, leaving iridium and osmium. Although iridum sells at about $6.25 per gram we import 5000 oz. annually.

Osmium.—Osmium is remarkable in having the greatest density, 22.5, of any substance known. It is gray like iron, but, unlike that metal, resists the attack of aqua regia. However, it unites easily with oxygen when heated, forming the tetroxide, OsO_4. This oxide is a white solid, slowly soluble in water. Its vapor is most unpleasant in odor and is extremely poisonous. It is called "**osmic acid**" but in reality is not an acid nor even a acid anhydride. The substance is used to stain tissues, which it does by its powerful oxidizing properties. Animal tissue reduces it to the black finely divided metal. At the same time the tissues are hardened.

Haber pronounced osmium the best catalyst for the synthesis of ammonia from nitrogen and hydrogen, and Welsbach invented an osmium filament lamp. However, it has been estimated that there are only a few hundred pounds of the element available on the earth. It may seem futile to discover new uses for an element too rare to supply any reasonable demand. Yet when man needs more of an element he usually discovers new sources, as he did with tungsten, radium, thorium, and vanadium.

Ruthenium.—Ruthenium resembles osmium, especially in the formation of the volatile tetroxide, RuO_4, made by fusing the metal with potassium hydroxide and potassium nitrate. The dioxide RuO_2 is formed by heating ruthenium in a current of oxygen and Ru_2O_3 by heating in air.

Summary.—" These metals find wide usage in four major fields: the chemical, electrical, dental, and jewelry industries. They are used in the manufacture of apparatus, catalyzers, electrodes, incandescent lamps, furnace coils, contact points, thermocouples, X-ray tubes, cautery points, chemical compounds, etc. The dental and miscellaneous uses have shown, within the past several years, an appreciable decline, leaving for the chemical, electrical, and jewelry uses an increase of well over 10,000 ounces a year. About 60 per cent of this is consumed by the jewelry industry and about 20 per cent each by the chemical and electrical industries. Of all the platinum metals used in the United States in 1926, 6.32 per cent was used by the chemical industries; 12.87 per cent by the electrical industries; 11.51 per cent by the dental manufacturers; 56.54 per cent went into jewelry; and 12.76 per cent was distributed over miscellaneous fields."

PRICES OF PLATINUM METALS IN 1930

Platinum	\$2.00 per gram
Iridium	6.27 " "
Palladium	1.13 " "
Osmium	1.77 " "

(Multiply by 31 for troy ounce price.)

EXERCISES

1. What is the per cent of potassium in potassium chloroplatinate, K_2PtCl_6?
2. How could you make K_2PtCl_4 from platinum?
3. What would you suggest as a substitute for platinum in the laboratory?

APPENDIX

HYDROGEN ION CONCENTRATIONS IN TERMS OF pH VALUES

"The normal and molar system of expressing the concentration of acids and bases does not distinguish between the quantity of H^+ ions actually present at a given dilution and the *potential* quantity of H^+ ions. The pH scale (of Sorensen) does this and indicates a measure of the actual concentration of the H^+ ions present in the solution."

Purely for convenience, then, values of the logarithms of the reciprocal of the H^+ concentration are obtained and arbitrarily termed "pH." For any solution containing H^+ we state that

$$\text{pH} = \log \frac{1}{(H^+)} \cdot$$

In order that the worker may have some idea of the degree of acidity corresponding to various pH values, it may be stated that a solution which has a pH value of 5.0 is 10 times as acid as one with a pH of 6.0. Analogously, a solution of pH 4.0 is 10 times as acid as one of pH 5.0. Thus pH 4.0 indicates an acidity 100 times as great as pH 6.0. A similar relationship holds on the alkaline side of the scale. That is, a solution which has a pH of 9.0 is 10 times as alkaline as one which has a pH value of 8.0, etc.

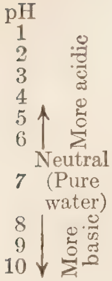
Water ionizes to a minute degree and its ionization constant can be determined.

$$\text{Conc. of H Ions} \times \text{Conc. of OH Ions} = \text{a Constant.}$$

By electrical conductivity measurements, this constant has been found to be 1/100,000,000,000,000 or 10^{-14} at 22° C. Since in pure distilled water the number of H ions is equal to the number of OH ions, each must have a concentration of 1/10,000,000 or 10^{-7}.

In the case of pure distilled water, in which the H ion concentration is* 0.0000001 *or N*/10,000,000, *the pH value would therefore be the log of* 1/0.0000001 *or of* 10,000,000, *which is* 7.0. *This value* 7.0 *is, therefore, the neutral point on the pH scale.

It will readily be seen that pH values below 7.0, such as 6.0, 5.0, etc., denote acidity, the degree of acidity increasing as the numbers decrease. For example, if a small amount of HCl is added to pure distilled water which has an H ion concentration of 10^{-7} or a pH value of 7.0, the acid will dissociate into positive H ions and negative Cl ions. The total number of H ions in the solution will, therefore, be greater than 10^{-7}, and the solution will therefore be acid. Suppose the H ion concentration is found to be N/1,000,000. The pH value will be the log of 1,000,000 which is 6.0. Similarly, if the H ion concentration is N/100,000, the pH value will be 5.0, etc. It should be remembered that, since we are dealing with logarithmic values, a solution having a pH value of 6.0 contains 10 times as many H ions as one having a pH value of 7.0. Similarly, a solution of pH 5.0 contains 100 times as many H ions as one of pH 7.0.



Since by the law of mass action

$$\text{Conc. of H Ions} \times \text{Conc. of OH Ions} = \text{a Constant},$$

it is apparent that as the H ion concentration increases the OH ion concentration must decrease, and vice versa. Even in a strongly alkaline solution there are, however, some H ions and, for the sake of simplicity, it is advisable to express both acidity and alkalinity in terms of pH values.

From the fact that neutral water has an H ion concentration of N/10,000,000, it is apparent that an alkaline solution must contain a smaller number of H ions. Let us assume that, by adding a small amount of sodium hydroxide to pure water, we decrease the H ion concentration to N/100,000,000. The pH value of this solution would be the log of 100,000,000 which is 8.0. Similarly, if the H ion concentration is reduced to N/1,000,000,000, the pH value would be 9.0. This shows why all values higher than 7.0 denote alkalinity, the degree of alkalinity increasing as the numbers increase. It should be remembered here also that a solution of pH 9.0 contains 10 times as many OH ions as one of pH 8.0.

It is therefore seen that the pH value is an absolutely accurate measure of the DEGREE of acidity or alkalinity of a solution.

The exact meaning of H ion concentration and pH values, and the derivation of the latter, can be made clear by a few concrete examples. An N/10 solution of hydrochloric acid is one which contains 3.65 g. of HCl or 0.1 g. of *ionizable* H per liter. Electrical conductivity measurements have shown that at 18° C., 91.4% of the HCl is dissociated. This means that 914 molecules out of every 1000 do not exist as molecules, but are split up into H and Cl ions. The remaining 8.6% of course exist as molecules. If the HCl were completely ionized, the N/10 solution would contain 0.1 g. of H ions per liter. Since, however, only 91.4% is ionized, it contains 0.1 × 0.914 = 0.0914 g. of H ions per liter. The normality of this solution with respect to H ions is $\frac{N}{1/0.0914}$ = N/10.94. The pH value of N/10 hydrochloric acid is, therefore, the logarithm of 10.94 or 1.04.

An N/10 solution of acetic acid also contains 0.1 g. of *ionizable* H per liter. Electrical conductivity measurements show, however, that at 18° C. it is dissociated only to the extent of 1.36%. Hence the hydrogen ion concentration is 0.1 × 0.0136 = 0.00136 g. per liter. This is equivalent to an N/735 solution of H ions. The pH value of N/10 acetic acid is therefore the log of 735, which is 2.86.

The titration values of 0.1 N solutions (equal volumes) of the following acids and bases are all the same, for as rapidly as any H^+ (or OH^-) ions are used up more molecules ionize, finally all of them. The actual quantity of H^+ ions or OH^- ions present in 0.1 N solutions differs widely from the weak acids and bases to the strong ones, as shown by the following table:

APPROXIMATE pH VALUES OF VARIOUS ACIDS AND BASES (0.1 N)

ACIDS	pH VALUE	BASES	pH VALUE
Hydrochloric acid	1.0	Sodium bicarbonate	8.4
Sulfuric acid	1.2	Borax	9.2
Phosphoric acid	1.5	Ammonia	11.1
Acetic acid	2.9	Sodium carbonate	11.6
Alum	3.2	Trisodium phosphate	12.0
Carbonic acid	3.8	Sodium metasilicate	12.2
Boric acid	5.2	Sodium hydroxide	13.0

These pH values may be determined by the Hydrogen Electrode (p. 552) or by use of a series of special indicators. In the following table Clark and Lubs show how to follow the range of pH values by trial with various indicators.

COMMON NAME	COLOR CHANGE ACID-ALKALINE	pH RANGE
Thymol blue (acid range)	Red-yellow	1.2–2.8
Brom phenol blue	Yellow-red	3.0–4.6
Methyl red	Red-yellow	4.4–6.0
Brom cresol purple	Yellow-purple	5.2–6.8
Brom thymol blue	Yellow-blue	6.0–7.6
Phenol red	Yellow-red	6.8–8.4
Cresol red	Yellow-red	7.2–8.8
Thymol blue (alkaline range)	Yellow-blue	8.0–9.6
Cresol phthalein	Colorless-red	8.2–9.8

"Buffer salts" such as sodium acetate not only decrease the H^+ concentration of very acid solutions, but stabilize it against any marked change due to addition of bases. Acid solutions are buffered by addition of salts of weak acids, sodium acetate, for example, while basic solutions are buffered by salts of weak bases such as ammonium chloride. Blood and fruit juices are buffered in their natural state.

The city of Milwaukee recently built a twenty-million dollar sewage disposal plant wihch depends upon the colorimetric determination of pH value for its successful operation. J. A. Wilson and his collaborators found that activated sludge can be freed from water most effectively when its pH value is lowered to 3.4 by the addition of acid. The filtrate from this sludge poisons the hydrogen electrode, but the pH value can be measured quickly and accurately by means of indicators. More than one million gallons of sludge per day, drawn from over 85 million gallons of sewage, are treated with ferric chloride or sulfuric acid, and the pH value is carefully adjusted to 3.4 before filtering. Without this adjustment, the plant could not operate. This sludge yields 100 tons per day of dry fertilizer, very rich in nitrogen, which is shipped to all parts of the country. Many other plants have adopted the Milwaukee pH control.

Wide experience in many different parts of the country has demonstrated that the most efficient coagulation takes place at a definite pH value, this value being different for different waters. For example, the optimum pH for different waters in one state varies from 4.2 to 7.6, when alum is used as a coagulant. This has been found to be due to variations in color, turbidity, natural alkalinity, and a number of other factors.

NOTE: Most of this section has been quoted direct from a pamphlet, *The ABC of Hydrogen Ion Control* by W. A. Taylor of the La Motte Chemical Products Company.

REFERENCES

"Applications of pH Control" (W. A. Taylor), *J. Chem. Ed.*, *6*, 36, (1929).

"Theory of pH Control and Methods Used" (Taylor), *Ind. Eng. Chem.*, *19*, 999, (1927).

MELTING POINTS OF METALS AND A FEW NON-METALS

Mercury	−38.9° C.	Silver	960.5° C.
Cæsium	+26.0°	Gold	1063.0°
Gallium	29.75°	Copper	1083.0°
Phosphorus	44.10°	Manganese	1260.0°
Potassium	62.3°	Beryllium	1350.0°
Sodium	97.5°	Silicon	1420.0°
Sulfur (rhombic)	112.8°	Nickel	1452.0°
Iodine	113.5°	Cobalt	1480.0°
Lithium	186.0°	Iron	1535.0°
Tin	232.0°	Chromium	1615.0°
Bismuth	271.0°	Vanadium	1710.0°
Cadmium	320.9°	Platinum	1755.0°
Lead	327.5°	Rhodium	1995.0°
Zinc	419.4°	Boron	2300.0°
Antimony	630.5°	Iridium	2350.0°
Magnesium	651.0°	Molybdenum	2620.0°
Aluminum	658.0°	Tantalum	2770.0°
Calcium	810.0°	Tungsten	3370.0°
Barium	850.0°	Carbon (graphite)	3500.0°

WEIGHT IN GRAMS OF 1 LITER OR VARIOUS GASES
(Standard conditions)

Air	1.2928	Hydrogen chloride	1.6392
Ammonia	0.7708	Hydrogen sulfide	1.5392
Argon	1.7838	Methane	0.7168
Carbon dioxide *	1.9768	Nitric oxide	1.3402
Carbon monoxide	1.2507	Nitrogen	1.2507
Chlorine	3.2140	Nitrous oxide	1.9777
Helium	0.1786	Oxygen	1.4290
Hydrogen	0.0898	Sulfur dioxide	2.9267

* The density of CO_2 referred to air is $\frac{1.9768}{1.293} = 1.53$.

SOLUBILITY PRODUCTS

The solubility product is the equilibrium constant for the saturated solution of a solid strong electrolyte.

ELECTROLYTE	K	ELECTROLYTE	K
HgCl	3×10^{-18}	$Fe(OH)_2$	2×10^{-14}
AgCl	1×10^{-10}	$Fe(OH)_3$	1×10^{-38}
AgBr	8×10^{-13}	$Mg(OH)_2$	2×10^{-11}
AgI	1×10^{-6}	$Mn(OH)_2$	4×10^{-14}
$BaCO_3$	8×10^{-9}	CuS	8×10^{-45}
$CaCO_3$	9×10^{-9}	CdS	1×10^{-29}
$SrCO_3$	2×10^{-9}	FeS	1×10^{-19}
		NiS	1×10^{-24}
$BaSO_4$	1×10^{-10}	ZnS	1×10^{-23}
$SrSO_4$	3×10^{-7}	HgS	1×10^{-53}

PRESSURE (OR TENSION) OF WATER VAPOR IN MILLIMETERS OF MERCURY

TEMPERATURE	PRESSURE	TEMPERATURE	PRESSURE
0°	4.6	21°	18.5
5°	6.5	22°	19.6
10°	9.1	23°	20.9
12°	10.4	24°	22.2
15°	12.7	25°	23.5
16°	13.5	26°	25.0
17°	14.4	27°	26.5
18°	15.3	28°	28.1
19°	16.3	29°	29.7
20°	17.4	30°	31.5

CONVERSION TABLE

Metric and English Systems

1000 millimeters (mm.)	= 1 meter	2.54 cm.	= 1 inch
100 centimeters (cm.)	= 1 meter	1 meter	= 39.37 inches
10 millimeters	= 1 cm.	1 liter	= 1.06 quarts
		1 gram	= 15.4 grains
1000 grams = 1 kilogram (Kg.)		1 kilo	= 2.20 pounds
1000 cubic centimeters	= 1 liter	28.35 grams	= 1 ounce av.
1 cu. ft.	= 28.32 liters	1 pint	= 16 fluid oz.
1 lb. av.	= 453.59 g.	1 teaspoon	= 4 cc.
1 oz. avoirdupois	= 28.35 g.	1 gallon (U. S.)	= 3785.4 cc.
1 liter = 1.0567 liquid quarts (United States)		1. gram	= 0.0353 oz.
		28.3495 gram	= 1. oz.
1. cm.	= 0.3937 in.	1. kilogram	= 2.2046 lb.
2.54 cm.	= 1. in.	0.4536 kilogram	= 1. lb.
1 meter	= 3.28 ft.	1 drop of water	= 1/20 cc.
0.3048 meter	= 1. ft.	1 teaspoonful	= 4 cc.
		1 tablespoonful	= 16 cc.
1. kilometer	= 0.6214 mi.	1 fluid ounce	= 29.57 cc.
1.6093 kilometer	= 1. mi.	1 cup	= 240. cc.

The metric system is essentially a decimal system, making calculations easier. As it is now, we in America are not consistent, for we use a decimal system of money, while machine shop practice deals with a thousandth of an inch as well as the half, quarter, eighth, etc.

It is interesting to note that the meter is about 10 per cent longer than the yard, the half-kilo (world pound) about 10 per cent heavier than the common pound, and the liter about 5 per cent larger than the quart.

A dime is about 1 mm. thick and weighs 2.5 grams.

THE COST OF CHEMICALS

Very Expensive	Iridium Platinum Palladium Gold
\$1.00–\$5.00	Silver nitrate Iodine Saccharin Bismuth Tungsten Cellulose acetate
\$0.50–\$1.00	Magnesium Cadmium Mercury Camphor Phosphorus
20–50 cents	Aluminum Tin Bromine Nickel Sodium Sodium peroxide Lead dioxide Tartaric acid
10–20 cents	Copper Butyl alcohol Olive oil Urea Glycerol Potassium permanganate Acetic acid, glacial Phenol Nitric acid
5–10 cents	Antimony Formaldehyde Linseed oil Methyl alcohol Litharge Cottonseed oil Sulfur dioxide, liquid Carbon tetrachloride Phosphoric acid Potassium hydroxide Sodium dichromate Zinc Denatured alcohol Lead Carbon dioxide, (solid) Carbon disulfide Copper sulfate
1–5 cents per pound	Ferrous chloride Manganese dioxide Liquid chlorine Ammonium hydroxide Benzene Sodium hydroxide Glucose Borax Sulfuric acid Hydrochloric acid Calcium chloride Lime Sodium silicate Sulfur Sodium chloride Iron (pig) Nitric acid

INDEX

References in **bold face type** are the most important.

- Absolute temperature, 50
  - zero, 50
- Acetic acid, 402
  - anhydride, 418
- Activated sludge, 636
- Acetone, 401
- Acetylene, 371
- Acidimetry, 222
- Acids, 216, 228
  - dibasic, 216
  - monobasic, 216
- Actinium, 274
- Adsorption, 464
- Air, a mixture, 284
  - separation of, 295
- Air ships, 81
- Alchemists, 15
- "Alclad" sheet, 563
- Alcohol, 397
  - absolute, 393
  - butyl, 413
  - ethyl, 395, **398**
  - from petroleum, 399
  - methyl, 395, **397**
  - solid, 468
- Aldehydes, 396, 400
- Alizarin, 569
- Alkali metals, 484
- Alkalimetry, 222
- Alkaline earth metals, 502
- Allotropy, 230
- Alloys, 477
  - table of, 480
- Aluminum, **551**, 562, 577
  - bronze, 560
  - blowpipe, 562
  - cables, 559
  - chloride, 565
    - anhydrous, 393, 572
  - hydroxide, 564
  - occurrence, 557
  - oxide, 563
  - paint, 560
  - preparation, 557
  - properties, 559
  - pure, 562
  - refining of, 563
  - story of, 572
  - tests for, **564**, 572
  - uses, 560
- Aluminothermy, 561
- Alums, 566
- Amalgams, 479
- Amides, 316
- Ammonia, 313
  - bomb, 324
  - burning, 315
  - chemical properties, 315
  - direct synthesis, 322
  - liquid, 156
  - physical properties, 314
  - preparation, 314
  - uses, 316
- Ammonium, **498**
  - amalgam, 316, 498
  - carbonate, 499
  - chloride, 318, 499
  - complexes, 319
  - hydroxide, 317, 498
  - nitrite, 499
  - nitrate, 318, 499
  - salts, 318
  - sulfate, 318, 499
  - sulfide, 500
  - tests, 500
- Ampere, 554
- Amphoteric, hydroxides, 536
- Amylase, 411
- Analysis, positive ray, 281
- Anhydrides, 30, 188
- Aniline, 381
- Anion, 204
- Anode, 203
- Antichlor, 254
- Antimony, **363**
  - history, 363
  - occurrence, 364
  - oxides, 364
  - preparation, 364
  - properties, 364
  - salts, 364
  - sulfides, 365
  - thio-salts, 365
  - trichloride, 365

- trioxide, 364
- uses, 364

Apparatus, fog track, 269
Appendix, 633
Aqua regia, 528
Arc process, 320
Argon, 292
- family, 292

ARISTOTLE, 15
ARRHENIUS, 206, 212
Arsenic, **359**
- acids, 362
- history, 359
- occurrence, 359
- oxides, 361
- preparation, 360
- properties, 361
- thio-acids, 363
- triiodide, 361
- trisulfide, 362, 461

Arsine, 362
Artichoke, 410
Artificial gems, 564
- silk, 419

Asbestos, 435, 529
Asphalt, 378
ASTON, 275, 280
Atmosphere, 284
Atomic numbers, 264, 265
- theory, 15
- weights, 126

Atoms, 16
- Bohr, 278
- structure of, 267, 274

AVOGADRO, 126
- number, 134

Babbitt metal, 479
Bacteria, 412, 311
Bakelite, 400, 420
Baking powders, 490
Baking soda, 490
Balanced rations, 423
Bases, 198, 217, 228
- monoacid, 217

Barium, **512**
- hydroxide, 513
- nitrates, 513
- occurrence, 512
- oxides, 512
- sulfates, 512
- tests, 513

Barite, 512
Barometer, 48
Bauxite, 558, 563
BECQUEREL, 267
Benzene, 379
BERGIUS, 387, 388, 415
Beryllium, 546
- hydroxide, 547

BERZELIUS, 10, 431
Bessemer converter, 607
- process, 606

Bicarbonates, 117
Bismuth, **366**
- compounds, 366
- occurrence, 366
- preparation, 366
- properties, 366
- subnitrate, 366

Blast furnace, 600, 601
- gas, 387

Blanc fixe, 512
Bleaching powder, 189
Blue prints, 617
Blue vitriol, 521
Bohr atom, 278
Boiling point, 60
- constant, 178
- rise, 150

Bomb calorimeter, 35
Bordeaux mixture, 521
Boric acid, 439
Boron, **438**
- occurrence, 439

Borax, **439**
- beads, 440

BRAGG, 66
Brick, 569
Brin process, 27
Bromine, 167, **168**
- uses, 172, 173

Brownian movement, 456
B.T.U., 389
Buffer salts, 636
BURTON, 375, 376
Butte, 516
By-product coke oven, 382

Cadmium, 540
- occurrence, 540
- properties, 540
- sulfide, 540
- tests, 540

Caesium, 500
Calcium, 502
- arsenate, 361
- bisulfite, 244

  bicarbonate, 508
  carbonate, 503, 508
  carbide, 122
  chloride, 507
  fluoride, 507
  hydroxide, 506
  oxide, 504
  occurrence of, 502
  preparation, 503
  properties, 503
  sulfate, 506
  tests, 512
Calomel, 543
Calorie, 33
Camphor, 418
  synthetic, 418
CANNIZZARO, 127, 258
Carbide, 114
Carbohydrates, 407, 422
Carbolic acid, 381
Carboloy, 625
Carbon, 109
  amorphous, 111
  black, 113
  chemical properties, 113
  cycle, 121
  dioxide, **114**, 115, 116, 118
  disulfide, 122
  monoxide, 118, 120
  physical properties, 113
  tetrachloride, 121
Carbonates, 117
Carbonic acid, 116
Carborundum, 123
Carnallite, 496, 529
Casale process, 323
CASTNER, 195, 557
CAVENDISH, 96, 292, 329
Cation, 204
Cathode, 204
  rays, 17
Catalyst, **39**, 28
  lattice, 67
  vanadium, 251
Catalytic process, 73
Cellulose, 407, 415
  nitrates, 416
  acetate, 418
Cementite, 605
Cementation steel, 609
Cement, 570
  alumina, 571
  Portland, 570, 572
Celluloid, 417
Charcoal, 112
Chemicals, cost, 640
Chemical change, 7
  affinity, 78
  reaction, types of, 165
  warfare, 174
Chemical warfare service, 166
Chemiluminescence, 453
Chili saltpeter, 168
Chlorates, 192
Chloric acid, 191
Chlorine, 158, 280
  chemical properties, 162
  history of, 158
  occurrence, 158
  preparation, 159, 161
  physical properties, 162
  tests for, 167
  uses of, 165
Chlorides, 162
Chloroform, 394
Chloroplatinic acid, 629
Chlorpicrin, 166
Chromates, 591
Chrome steel, 613
Chrome tanning, 591
Chromium, 586
  chromite, 586
  ferrochrome, 586
  metallurgy, 586
  occurrence, 586
  plating, 587
  salts, 588
  tests, 592
Chromous compounds, 589
Chromic compounds, 590
  alum, 590
  chloride, 590
  hydroxide, 590
  salt solutions, 590
Cinnabar, 540
Claude process, 323
Coagulation, 466
Coal, 112
  derivatives, 379
  gas, 384
  powdered, 388
  tar, 381
Cobalt, 617
  hydroxides, 617
  occurrence, 617
  oxides, 617
  properties, 617
  salts, 618

  sulfide, 618
  tests, 620
Coke, 111
Coking, 383
  low-temperature, 383
Colloidal state, 454
  arsenic sulfide, 462
  garden, 154
  gold, 461
  silver, 461
Colloids, 454
  preparation, 457, 458, 461
  protective, 467
Colloid chemistry, 454
  applications of, 471
  mills, 458
Column stills, 398
Combustion, 31
Combining weights, 10
Common ion effect, 305
Complex cyanides, 616
Complex salts, 566
Compounds, 4
Concrete, 571
Conductivity and ionization, 213
Contact process, 249
Counter current principle, 170
Conversion table, 639
Coolidge, 282
Coördinate links, 278
Copper, 515
  ammonia compounds, 521
  complex cyanides of, 522
  converters, 516
  leaching, 518
  metallurgy, 515
  matte, 516
  occurrence, 515
  properties, 519
  refining, 517, 518
  tests for, 522
Copper on glass, 528
Corrosive sublimate, 544
Cosmic rays, 450
Cost of chemicals, 640
Cottrell process, 357, 470
Coulomb, 554
Cracking, 375, 376
Creosote, 383
Critical pressure, 29
  temperature, 29, 59
Crookes, 17
Crucible steel, 609
Cryolite, 169
Crystal lattice, 482
  structure, 66
  systems, 64
Cupric oxide, 520
  cyanides, 521
  hydroxide, 520
  sulfide, 521
  sulfate, 521
Cuprous chloride, 520
  oxide, 520
Curie, Madame, 268
  Pierre, 269
Cyanamid process, 321
Cyanogen, 124
Cyanates, 124
Cyanides, 124

Dakin's solution, 188
Dalton, 15, 126
Daniell cell, 553
Davy, 158, 167, 195, 328, 496, 503
Debye-Hückel theory, 211, 307
Dehydrite, 533
Deliquescence, 150
Density, 97
  of gases, 637
Deville, 557
Dewar, 291
  Dewar bulb, 290
Dialysis, 462
Dialyzers, 463
  collodion, 463
  sausage skin, 463
Diamond, 109
Dichromates, 591
Diffusion of gases, 55
Digestion, 422
Distillation, 60
  curve, 62
  fractional, 61
Distribution law, 144
Döbereiner's triads, 259
Double salts, 566
Dry cells, 499
Dry ice, 118
Duco, 418
Dumas, 130
Duralumin, 479, 561
Duriron, 334, 613
Dust, 470
  explosions, 39, 46, 286
Dyeing, 567, 568
Dyes, 567
  acid, 568

  alizarin, 569
  direct, 568
  indigo, 567
  mordant, 568
Dynamite, 339, 417

Edison storage cell, 585, 620
Efflorescence, 100
Electric cells, 549
  energy, 553
  furnace, 612, 621
Electrochemistry, 548
Electrolysis, 72, 203
Electrolytes, types of, 216
Electrometric titration, 553
Electromotive force, 550
  series, 225, 549
Electrons, 18, 93, 208, 277, 548
  orbits, 279
Elements, 4
  allotropic forms of, 44
Emulsoid state, 463
Emulsions, 135, 459
  types of, 460
Enamels, 438
Endothermic, 33
Energy, 3
Enzymes, 411, 412
Epsom salts, 529, **532**
Equations, 22
  electronic balancing of oxidation, 181, 341
Equilibrium, 80, 297
  constant, 302, 303
Esters, **402,** 403
Ethanol, 398
Ethereal salts, 402
Ethers, 400
Ethylene, 370
Ethyl gas, 173
Ethyl group, 394
Eutectic, 478
Exothermic, 33
Explosives, 339, 417

Faraday, 162, 203, 291
Farm wastes, 420
Fats, 403, 421
  hardened, 73, 81
Fauser process, 323
Fehling's solution, **520**
Feldspar, 569
Fermentation, 411
Ferrates, 616
Ferric compounds, 615
  chloride, 616
  hydroxide, 615
  oxide, 615
Ferrous compounds, 614
  chloride, 614
  sulfate, 614
Films, 469
Fischer, 388
Flame, 390
  atomic hydrogen, 82
Fluorescence, 443
Fluorine, 167, **169,** 174
  preparation, 169
  properties, 171
Fluorspar, 169, 172
Flux, 516
Food and nutrition, **421**
  chart, 429
  fuel value, 423
Formaldehyde, 400
Formic acid, 402
Formulas, 21
Frasch, 230
Frazer, 155
Freezing point lowering, 147, 201, 202
Froths, 469
Fuels, **389,** 390
  liquid from coal, 387
  powdered coal, 388
Furfural, 401, 420

Galena, 577
Galvanizing, 535
Gas (and gases), 48
  blast furnace, 387
  coal, 384
  density of, 637
  kinetic theory of, 55
  liquefaction of, 63, 291
  marsh, 369
  mustard, 166
  natural, 369
  oil, 387
  poison, 166
  producer, 386
  rare, 261
  tear, 166, 261
  warfare, 166, 174
  water, 73, **385**
Gasolene, 369, 374
  casing-head, 369
  high-test, 369
  statistics, 380

Gayley dry blast, 603
Gay-Lussac, 78, 126, 127, 167
  tower, 245
Gels, 467
Glass, 436, 441
  cut, 185
  pyrex, 438, 441
  ruby, 258
  structure of, 67
Glover tower, 245
Glucinum, 546
Glucose, 409
Glycerine, 399
Glycol, 399
Goitre, 168
Gold, 526
  metallurgy, 527
  properties, 527
  production, 527
Goldschmidt process, 561
Graphite, 110
Gravity cell, 550
"Green Leaf Laboratory," 447
Gunpowder, 497
Gypsum, 253, 506

Haber process, 322
Hafnium, 264, 585
Hall, Charles M., 557
Halogen family, **158**
  acids, 180
    catalytic preparation of, 183
    properties of, 184
    uses of, 185
  occurrence, 168
  oxygen acids of, 187
  tests, 185
  uses, 172
Hardness of water, 508
  permanent, 508
  temporary, 508
Hare, 77
Heat of combustion, 33
  formation, 34, 184, 220, 561
  fusion, 63
Heat insulation, 532
Helium, 269, 271, 293, 296
Hevesy, 264
Hill, 41
Hillebrand, 293
Holland, 155
Holmes-Manley cracking still, 377
Homologous series, 368
Hoopes process, 562, 563
Hopcalite, 119
Hot-cathode tube, 282
Hopkins, 266
Humidity, 287
Hydrazine, 319
Hydrazoic acid, 319
Hydrates, 99
Hydrocarbons, 74, 367
Hydrides, 77
Hydrofluoric acid, 185
Hydrogen, 70
  atomic, 81
  chemical properties, 76
  history, 70
  manufacture of by
    catalytic process, 73
    liquefaction process, 73
    steam-iron process, 74
  occurrence, 70
  para, 76
  physical properties, 75
  preparation of, 70
  purification of, 75
  uses, 81
Hydrogenation, 81
Hydrogen bromide, 180
Hydrogen chloride, 175
  chemical properties, 178
  history, 175
  physical properties, 178
  preparation, 175
  tests for, 180
  uses, 179
Hydrogen electrode, 551, 552
Hydrogen iodide, 181
Hydrogen peroxide, **104**
  preparation, 105
  properties, 105
  tests for, 108, 106
Hydrogen sulfide, 235
  chemical properties, 237
  cracking of, 237
  physical properties, 236
  preparation, 236
  uses, 237
Hydrolysis, 223, 351
Hydroxylamine, 319
Hypochlorous acid, 187

Illinium, 266
Indicators, 223, 335
Indigo, 567, **569**
Ink, 614
Insecticides, 367

Inulin, 410
Invert sugar, 409
Iodine, 167, **168**
Iodoform, 173
Ionic displacement, 548
Ionic equilibrium, 303
Ionic theory, 206
  reactions in liquid phosgene, 226
    ammonia, 227
Ionization, 200
  and conductivity, 213
  complete, 211
  equilibrium, 209
  fraction ionization, 214
  of fused salts, 210
Ionogen reactions, 219
Ions, velocity of migration, 210
Iridium, 631
Iron, 599
  complex cyanides of, 616
  metallurgy, 600
  occurrence, 599
  pig, 605
  properties, 611
  pure, 611
  rustless, 614
  rustproofing, 611
  stainless, 614
  tests for, 617
  wrought, 605
Isobares, 281
Isoelectric point, 466
Isomorphous, 65
Isotopes, 273, 280

Javelle water, 188, 190
Joule, 554

Kaolin, 569
Katanga, 274
KEESOM, 50, 293
KELLY, 607
Kerosene, 374
Ketones, 401
Kinetic theory, 55
KNIETSCH, 249
Krypton, 295

Lacquers, 417
Lakes, 569
Lampblack, 113
LANGMUIR, 82
LAUE, 66
LAVOISIER, 25, 32
  experiment, 26, 32
Law
  of Avogadro, 59, 126
  of Boyle, 48
  of Charles, 50
  of conservation of energy, 3
  of conservation of mass, 8, 16
  of Dalton, 143
  of definite composition, 8, 9, 16
  of definite proportions, 8
  of distribution, 144
  of Dulong and Petit, 133
  of Faraday, 207
  of Gay-Lussac, 78
  of Graham, 54
  of Henry, 143
  of mass action, 301
  of partial pressures, 53, 143
  of multiple proportions, **12,** 16
  of Raoult, 150
  of van't Hoff, 300
Lead, **577**
  chamber process, 245, 247
  chloride, 582
  dioxide, 581
  halides, 582
  iodide, 582
  metallurgy, 578
  monoxide, 581
  occurrence, 577
  oxides, 581
  properties, 579
  pyrophoric, 39
  red, 581
  refining, 578
  storage battery, 583
  uses, 580
  white, 583
Leather manufacture, 406
  artificial, 418
LeBlanc process, 487
LeChatelier's principle, 300
Leprosy, 404
Levulose, 410
LEWIS, 275
LIEBIG, 495
Light octaves, 442
  quanta, 443
  chemical effects of, 443
  ultra violet, 443, **448**
Lignin, 244
Lime, uses of, 505
Lime-sulfur, 239
Liquid air, 289
  apparatus for, 290

  plant, 291
Liquids, 59
Liquefaction process, 73
Litharge, 581
Lithium, 484
  perchlorate, 137
Lithopone, 539
Lye, 496

Magnesia alba, 532
Magnesite, 529
Magnesia cements, 532
Magnesia mixture, 533
Magnesium, 529
  alloys, 531
  ammonium phosphate, 533
  carbonate, 532
  cements, 532
  chloride, 531
  hydroxide, 531
  occurrence, 529
  oxide, 531
  perchlorate, 533, 547
  phosphate, 533
  preparation, 529
  properties, 530
  sulfate, 532
  tests, 534
Manganese, 592
  dioxide, 594
  metallurgy, 593
  occurrence, 593
  properties, 593
  salts, 594
  steel, 613
  tests, 598
Manganous compounds, 594
Malt, 411
Maltase, 411
Marine borers, 166
Marsh gas, 369
Marsh test, 360
Masurium, 264
Mass, 2
  change to energy, 282
Matches, 349, 367
MATHERS, 167
Matte, 516, 578, 618
Matter, 2
Meker burner, 392
Melting point, 63
  of metals, 637
  curves, 478
MENDELEJEFF, 259
Mercury, 540
  amalgams, 541
  boiler, 542
  fulminate, 545
  metallurgy, 541
  occurrence, 540
  poisoning, 542
  properties of, 541
  purification, 541
  tests for, 545, 547
  vapor lamps, 541
Mercuric compounds, 544
  chloride, 544
  fulminate, 545
  iodide, 544
  nitrate, 545
  oxide, 544
  sulfate, 545
  sulfide, 545
Mercurous compounds, 543
  chloride, 543
  nitrate, 543
  oxide, 543
  sulfate, 543
Metals, 30, **474**
  activity series, 82
  bearing, 480
  crystal structures of, 476
  expansion coefficients, 476
  extraction from ores, 475
  occurrence, 475
  rare earth, 260
  solid solution, 482
Metaphosphoric acid, 353
Metastannic acid, 577
Methane, 369
Methanol, 397
Methyl group, 394
Metric system, 639
MEYER, 259
Microscopy of steel, 610
MILLIKAN, 17, 450
Minerals, silicates, 435
Minium, 581
Molar volume, 129
MOISSAN, 110, 167
Molecules, 16
Molybdenum, 622
  compounds, 622
Molybdic acid, 622
Monel metal, 618
Mordants, 567, 568
MORLEY, 78, 97
MORSE, 155

Mortar, 506
Moseley, 266

Naphtha, 374
Naphthalene, 382
Nelson cell, 197
Neon, 295
  glass tubes, 296
Nessler's solution, 545
Neutral salt effect, 211
Neutralization, 199, 220
Newlands, 259
  octaves of, 259
Nichrome, 587
Nickel, 618
  carbonyl, 619
  compounds, 619
  occurrence, 618
  properties, 618
  steel, 613
  tests for, 620
Niter cake, 334
Niton, 271
Nitrates, 332, 342
  tests for, 342
Nitric acid, **333**
  action on metals, 337
    metallic oxides, 338
    non-metals, 337
    organic compounds, 338
  oxidation by, 339, 340
  preparation of, 333
    arc process, 335
    Ostwald ammonia process, 336
    properties of, 337
    plant, 334
Nitric oxide, 329
Nitrided steel, 614
Nitrites, 342
Nitrogen, 309
  chemical properties, 311
  cycle, 312
  dioxide, 329
  fixation, 320
  fixation by bacteria, 325
  fixed, 313, 325
  history, 309
  occurrence, 309
  oxides of, 328
  pentoxide, 330
  physical properties, 311
  preparation, 310
    from coal, 313
  trichloride, 319
  trioxide, 330
  uses, 312
  world supply of, 325
Nitrocellulose, 417
Nitrobenzene, 339
Nitro compounds, 339
Nitroglycerine, 338, 339
Nitrosyl sulfuric acid, 248
Nitrous acid, 342
Nitrous oxide, 328
Non-metals, 30
Non-polar, 277
Normal potentials, 550
Nut margarine, 404
Nutrition, 430

Octet theory, 275
Oerstedt, 557
Oil, chaulmoogra, 404
  cotton seed, 404
  linseed, 404
  soya bean, 404
  tung, 404
Oil gas, 387
Oil of vitriol, 252, 254
Old Dutch process, 583
Olein, 403
Oleomargarine, 404
Onnes, 50, 292, 293
Open-hearth process, 608
Ore Flotation, 469
Organic acid, 396
Organic nitrates, 339
Orthophosphoric acid, 352
Osmic acid, 631
Osmium, 631
Osmotic pressure, 151
Ostwald, 206
Oxidation, **35**, 78, 93, 94, 340
Oxidation and reduction, 554
Oxidation at a distance, 555
Oxides, 31
Oxidizing agents, 597
Oxygen, **25**
  carbon dioxide balance, 285
  chemical properties, 29
  debt, 41
  occurrence, 26
  physical properties, 29
  preparation, 26
  tree, 37
  uses of, 36
Oxyhydrogen blowpipe, 77
Ozone, 41

  history, 41
  occurrence, 42
  preparation, 43
  properties, 42
  tests for, 45, 46
  uses, 45

Paint, drying of, 36
  white lead, 583
Palladium, 630
Palmitin, 403
Paper, sizing, 567
Paraffin, 374
Para hydrogen, 76
Parkes process, 523
Pentane, 374
Pentathionic acid, 240, 255
Peptization, 458
Perchlorates, 193
Periodates, 194
Periodic system, 256, 258
Permanganates, 596
Permalloy, 619
Perminvar, 619
Permutit, 510, 511
Peroxides, 107
Persulfuric acid, 254
Petroleum, **372,** 393
  coke, 374
  ether, 374
  production, 373
pH values, 228, 552, **633**
Picric acid, 381
Pig iron, 605
Pitchblende, 625
Phenol, 381
Phlogiston, 32
Phosgene, 120, 121, 174, 226
Phosphate, 354
  disodium, 354
  fertilizers, 358
  monosodium, 354
  rock, 358
  tests for, 356
  trisodium, 354
Phosphine, 357
Phosphoric acids, 351
Phosphorus, 346
  acids of, 351
  furnace, 347
  history, 346
  occurrence, 347
  pentachloride, 350
  preparation, 347
  properties, 348
  red, 348
  trichloride, 350
  white, 348
Photochemistry, 442
  of plants, 446
Photoelectric cell, 450
Photoelectrons, 450
Photography, **444,** 453
Physical change, 7
Pigments, 582
Plant food, 326
Plaster, 506
Plaster of Paris, 253, 506
Plastizers, 418
Platinum, 627
  compounds, 628
  chloride, 628, 629
Platinum metals, prices, 632
Polar compounds, 278
Polonium, 268
Polysulfides, 239
Polythionic acids, 255
Porcelain, 569
Portland cement, 570, 572
Positive ray analysis, 281
Potentials, normal, 550
  of metals, 552
Pottery, 569
Potash, 495
Potassium, 494
  bromide, 496
  carbonate, 497
  chloride, 496
  chlorate, 192
  cyanide, 497
  hydroxide, 497
  iodide, 496
  manganate, 595
  nitrate, 497
  occurrence, 494
  permanganate, 596
  preparation, 496
  properties, 496
  tests, 497
  triiodide, 172
Precipitation conditions, 305
Precipitation, electrical, 470
Pressure of water vapor, 638
Price of chemicals, 640
PRIESTLEY, 25, 46, 314, 328
Primary cell, 549, 556
Problems, solving, 83
Producer gas, 386

Properties, 6
Protein, 421
Proton, 18
Prussic acid, 493
Prussian blue, 616, 617
Puddling furnace, 605
Pyrex glass, 438, 441
Pyrophosphoric acid, 353
Pyrosulfuric acid, 254
Pyroxylin, 417

Quantum, 443
Quartz, 434
  fused, 434

Radicals, 89
Radium, **268,** 625
  decay of, 272
  disintegration, 271
  energy of, 273
  industry, 274
  services, 272
  uses of, 273
Radioactivity, 267
Radon, 271
Raleigh, 292
Ramsay, 271, 292
Raoult, 150
Rare earth metals, 260
Rasorite, 439
Rayon, 415, **419**
  statistics, 419
Rays,
  alpha, 269
  Becquerel, 267
  beta, 270
  cosmic, 450
  gamma, 271
  radium, 269
  Röntgen, 267
  ultra-violet, 443
Reaction, speed of, 38
  reversible, 78, 79
Reduction, **78,** 93, 94, 340, 554
Red phosphorus, 348
Refrigeration, 319
  plant, 317
Reverberatory furnace, 516, 605
Review suggestions, 47, 86
Rhenium, 264
Rhodium, 631
Richards, 132
Röntgen rays, 267
Rubber, 233
  synthetic, 393
Rubies, artificial, 564
Rubidium, 500
Rustproofing, 611
Ruthenium, 632
Rutherford, 271, 275

Saccharine, 408
Safety lamp, 392
Sal soda, 486
Salts, 186, 217, 228
  buffer, 636
  complex, 566
  double, 566
Salt, products from, 487
Scheele, 25, 158, 235, 445
Searles lake, 495
Selenides, 257
Selenium, 257
Sewage, 104
  disposal, 108
Shale oil, 314, 378
Silver, 523
  amalgamation, 523
  bromide, 525
  chloride, 525
  frosted, 524
  halides, 525
  iodide, 525
  leaching, 523
  metallurgy, 523
  nitrate, 526
  occurrence, 523
  oxide, 525
  oxidized, 524
  properties, 524
  tests, 526
  uses, 524
Silica, 433
Silicate minerals, 435
Silicic acids, 433
Silicon, 431
  occurrence, 431
  preparation, 431
  properties, 432
  tetrachloride, 432
Slag, 601, 606
Smoke, 388, 470
Soaps, **468,** 404
  cleansing action of, 465
Soapstone, 435, 529
Soddy, 271, 280
Sodium, **195**
  arsenate, 363
  arsenite, 363
  bicarbonate, 490

  - bromide, 486
  - carbonate, 486
  - chloride, 485
  - cyanide, 492
  - fluoride, 486
  - hydroxide, 196
    - statistics of, 198
  - hyposulfite, 255
  - iodide, 486
  - iodate, 168
  - molybdate, 622
  - nitrate, 493
  - nitrite, 493
  - perborate, 494
  - peroxide, 28
  - phosphate, 493
  - preparation of, 195
  - properties of, 196
  - pyrophosphate, 355
  - statistics, 489
  - sulfate, 491
  - sulfide, 492
  - sulfite, 491
  - tests for, 494
  - thioarsenate, 363
  - thioarsenite, 363
  - thiosulfate, 491
  - tungstate, 624
- Softening water, 508
- Soil fertility, 325
- Solder, 479
- Solubility product, 306, 538, 638
- Solubility,
  - curves, 142
  - measuring of, 139
  - temperature effect, 139
- Solute, 137
- Solutions, 135
  - colloid, 136
  - colors of, 218
  - cooling, 149
  - low-freezing, 148
  - molar, 145
  - normal, 145, 146
  - saturated, 138
  - solid, 137
  - standard, 221
  - supersaturated, 138
  - surface tension of, 156
- Solvay process, 487
- Solvent, 137
- Specific heat, 97
- Spectra, 452
  - bright-line, 452
  - dark-line, 452
- Spectroscope, 451
  - mass, 281
- Spiegeleisen, 593
- Spinthariscope, 270
- Spontaneous combustion, 36
- Spray drying, 101, 108
- Stacks, 604
- Stains, removal of, 614
- Stainless iron, 614
  - steel, 614
- Stannic compounds, 576
  - acid, 576
  - chloride, 576
  - tests, 576
- Stannous compounds, 575
  - chloride, 575
  - hydroxide, 575
  - oxide, 575
  - sulfide, 576
- Starch, 407
- Stassfurt, 159, 495, 529
- Steam-iron process, 74
- Stearin, 403
- Steel, **606**
  - alloy, 612
  - cementation, 609
  - chrome, 613
  - crucible, 609
  - heat treatment of, 611
  - manganese, 613
  - nickel, 613
  - nitrided, 614
  - rustproofing of, 611
  - stainless, 614
  - statistics of, 608
  - temper colors, 612
  - tungsten, 613
  - vanadium, 613
- Stellite, 587
- Sternutatory, 166
- Stibine, 365
- Stibnite, 364
- Still, column, 398
- Storage batteries, 556
- Storage cells, **583**, 585
- Stoves, 604
- Strontium, 513
  - hydroxide, 514
  - occurrence, 513
  - nitrate, 513
  - tests, 514
- Structural formula, 91, 343
- Sublimation, 64

- Sucrose, 408, 409
- Sugars, 408
- Sulfates, 253
- Sulfites, 244
- Sulfur, **229**
  - chemical properties, 232
  - distribution of, 235
  - occurrence, 229
  - physical properties, 230
  - preparation, 230
  - statistics, 235
  - uses, 233
- Sulfur dioxide, **241**
  - chemical properties, 243
  - physical properties, 242
  - preparation, 241
  - uses, 243
- Sulfur trioxide, 244
- Sulfuric acid, **244**
  - nitrosyl, 248
  - oil of vitriol, 252
  - persulfuric, 254
  - properties of, 252
  - pyrosulfuric, 254
  - statistics, 253
  - thiosulfuric, 254
  - uses, 253
- Sulfurous acid, 243
- Suspension, 135
- Suspensoid state, 463
- Surface tension, 62, 156
- Sweetness, 408
- Symbols, 21
- Sympathetic ink, 618
- Synthol, 388

- Tantalum, 625
- Tartar emetic, 364
- Tellurium, 258
- Tellurides, 257
- Temperature paints, 545
- Temper colors, 612
- Tetraethyl lead, 173
- Thermit process, 562
- Thiocyanates, 124
- Thiosulfuric acid, 254
- Tin, 573
  - disease, 574
  - metallurgy, 573
  - occurrence, 573
  - properties, 573
  - tests for, 577
- Titanium, 613
- Titration, 221
- T. N. T., 338, 381
- Toluene, 381
- Transition points, 141
- Tungsten, **623**, 626
  - carbide, 625
  - compounds, 624
  - lamp filaments, 624
  - properties, 623
  - steel, 613, 624
- Turnbull's blue, 616, 617
- Twitchell process, 405

- Ultra-violet light, 448
- Uranium, 625
- Urea, 414

- Vacuum, high, 49
- Valence, **87**
  - definition, 88
  - positive and negative, 92
  - primary and secondary, 92
- Vanadium, 621
  - catalyst, 251
  - steel, 613
- Van der Waal's equation, 58
- Van't Hoff, 155, 206
- Vapor pressure of solids, 64
- Vapor tension, 100
- Vaseline, 374
- Ventilation, 288
- Vinegar, 402
- Viscose silk, 420
- Viscosity, 62
- Vitamins, 424, 430
  - identification, 428
  - influences, 428
  - table, 427
- Vitriols, 254, 521

- Water, 96
  - boiling point of, 100
  - chemical properties, 98
  - gas, 73, 385
  - hardness of, 508
  - history, 96
  - natural, 102
  - occurrence, 96
  - of crystallization, 99
  - of hydration, 99
  - physical properties, 96
  - purification, 103
  - softening, 508
  - vapor tension of, 638
- Water gas, 73, 385

Water glass, 433, **434**, 435
Water softening, 514
Watt, 554
Weights, combining, 10
  equivalent, 146
  exact atomic, 131
  molecular, 126
Weight factor, 84
Welsbach mantles, 392
Werner's coördination theory, 629
Whisky, 411
White lead, 582, **583**
White phosphorous, 348
Winter hardiness of plants, 149
WÖHLER, 557
WOODHOUSE, 496
Wood's metal, 479
Wrought iron, 605

Xenon, 295

X-ray, 267
  spectra, 66

Yeast, 327

Zinc, 534
  chart, 539
  chloride, 537
  galvanizing, 535
  hydroxide, 536
  metallurgy, 534
  occurrence, 534
  oxide, 536
  properties, 535
  sherardizing, 535
  sulfide, 538
  tests, 539
  uranyl acetate, 494
  uses, 535, 539
Zymase, 411

Coulombs. At Wt
Valence.

Periodic Table showing Atomic Numbers in Red

Period	Group 0	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
0		1 H 1.008							
I	2 He 4.002	3 Li 6.940	4 Be 9.02	5 B 10.82	6 C 12.000	7 N 14.008	8 O 16.000	9 F 19.00	
II	10 Ne 20.183	11 Na 22.997	12 Mg 24.32	13 Al 26.97	14 Si 28.06	15 P 31.02	16 S 32.06	17 Cl 35.457	
III	18 A 39.94	19 K 39.10	20 Ca 40.07	21 *Sc* 45.10	22 *Ti* 47.9	23 *V* 50.96	24 *Cr* 52.01	25 *Mn* 54.93	26 *Fe* 27 *Co* 28 *Ni* 55.84 58.94 58.69
		29 *Cu* 63.57	30 *Zn* 65.38	31 *Ga* 69.72	32 *Ge* 72.60	33 As 74.96	34 Se 79.2	35 Br 79.916	
IV	36 Kr 82.9	37 Rb 85.44	38 Sr 87.63	39 *Y* 88.92	40 *Zr* 91.22	41 *Cb* 93.1	42 *Mo* 96.0	43 *Ma* ?	44 *Ru* 45 *Rh* 46 *Pd* 101.7 102.91 106.7
		47 *Ag* 107.880	48 *Cd* 112.41	49 *In* 114.8	50 *Sn* 118.70	51 Sb 121.77	52 Te 127.5	53 I 126.932	
V	54 Xe 130.2	55 Cs 132.81	56 Ba 137.36	57-71 Rare-Earths	72 *Hf* 178.6	73 *Ta* 181.5	74 *W* 184.0	75 *Re* 188.7	76 *Os* 77 *Ir* 78 *Pt* 190.8 193.1 195.23
		79 *Au* 197.2	80 *Hg* 200.61	81 *Tl* 204.39	82 *Pb* 207.22	83 Bi 209.00	84 Po 210.0	85	
VI	86 Rn 222.0	87	88 Ra 225.97	89 Ac ?	90 Th 232.12	91 U-X ?	92 U 238.14		

The *atomic number* appears before the symbol of each element in red and the *atomic weight* below. The atomic weights of Po, Ac, and U-X are uncertain values. With atomic numbers 81–84 and 88–92 are to be assigned a number of other elements, for the most part radioactive, which have the same chemical properties as the element in the table but somewhat different atomic weights.

Grown 1929

International Table of Atomic Weights of the Chemical Elements

relative

	Symbol	At. number	At. weight		Symbol	At. number	At. weight
Aluminum	Al	13	26.97	Molybdenum	Mo	42	96.0
Antimony	Sb	51	121.77	Neodymium	Nd	60	144.27
Argon	A	18	39.94	Neon	Ne	10	20.183
Arsenic	As	33	74.96	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N 2	7	14.008
Beryllium	Be	4	9.02	Osmium	Os 2	76	190.8
Bismuth	Bi	83	209.00	Oxygen	O	8	16.000
Boron	B	5	10.82	Palladium	Pd 2	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	31.02
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.07	Potassium	K	19	39.10
Carbon	C	6	12.000	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Radium	Ra	88	225.97
Cesium	Cs	55	132.81	Radon	Rn	86	222.
Chlorine	Cl	17	35.457	Rhenium	Re	75	188.7
Chromium	Cr 2	24	52.01	Rhodium	Rh	45	102.91
Cobalt	Co	27	58.94	Rubidium	Rb	37	85.44
Columbium	Cb	41	93.1	Ruthenium	Ru	44	101.7
Copper	Cu	29	63.57	Samarium	Sm	62	150.43
Dysprosium	Dy	66	162.46	Scandium	Sc	21	45.10
Erbium	Er	68	167.64	Selenium	Se	34	79.2
Europium	Eu	63	152.0	Silicon	Si	14	28.06
Fluorine	F	9	19.00	Silver	Ag	47	107.880
Gadolinium	Gd	64	157.26	Sodium	Na	11	22.997
Gallium	Ga	31	69.72	Strontium	Sr	38	87.63
Germanium	Ge	32	72.60	Sulfur	S	16	32.06
Gold	Au	79	197.2	Tantalum	Ta	73	181.5
Hafnium	Hf	72	178.6	Tellurium	Te	52	127.5
Helium	He	2	4.002	Terbium	Tb	65	159.2
Holmium	Ho	67	163.5	Thallium	Tl	81	204.39
Hydrogen	H 1	1	1.0078	Thorium	Th	90	232.12
Indium	In	49	114.8	Thulium	Tm	69	169.4
Iodine	I	53	126.932	Tin	Sn	50	118.70
Iridium	Ir	77	193.1	Titanium	Ti	22	47.9
Iron	Fe	26	55.84	Tungsten	W	74	184.0
Krypton	Kr	36	82.9	Uranium	U	92	238.14
Lanthanum	La	57	138.90	Vanadium	V	23	50.96
Lead	Pb	82	207.22	Xenon	Xe	54	130.2
Lithium	Li	3	6.940	Ytterbium	Yb	70	173.6
Lutecium	Lu	71	175.0	Yttrium	Y	39	88.92
Magnesium	Mg	12	24.32	Zinc	Zn	30	65.38
Manganese	Mn	25	54.93	Zirconium	Zr	40	91.22
Mercury	Hg	80	200.61				

atomic weights are relative weights of the atoms compared with oxyg

8 O X will combine with = 16.